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REFERENCE

Lane, B. H., 1935, Suggestions to authors of papers submitted for publication by the United States Geological Survey: U. S. Geol. Survey, Washington, D. C. (For sale by Superintendent of Documents, Washington, D. C. 35c.)

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GRANITE AGAIN

R. PERRIN

ABSTRACT. The "extreme transformist position" of the author on the formation of granites is not a matter of personal psychology. He sets forth the reasons why, in view of the present knowledge and geological observations, it is scientifically certain that a large number of granites have been formed by replacement in the solid and very unlikely that other granites may have originated from direct crystallization of magmas. This origin is admitted only if conclusive evidence compels recognition thereof.

The fact that a granite is "disharmonious"—using Walton's very good word—is not a proof that it is magmatic, as there are such granites for which, on the contrary, we find numerous evidences of replacement in situ. The strongest features in favor of magmatic origin are: (1) the intrusive character with sharp borders, but many observations have now shown the formation by replacement of apophyses or dikes of granite, aplite, or pegmatite with sharp borders; (2) the existence in the granite of so-called "displaced" inclusions, but in many cases observed or known, this existence is accounted for by the formation of granite by replacement. Rheomorphism or diapirism of granitic rocks is not to be set aside, a priori, although it meets with strong objections, but, to date, the author is not aware of cases where observations require the hypothesis of rheomorphism or diapirism without possible explanation by replacement in situ.

A few remarks have been added on the mechanism of metamorphism and granitization.

It is the hope of the author that his paper will be of some use to field observers, as such detailed field study will enable them to reach conclusions.

I have read with great interest the recent article in which Matt Walton (1955) outlines his views on the granite problem, basing himself on the extreme transformist viewpoint which I had briefly set forth in this JOURNAL (1954b). Mr. Walton has clearly defined the present state of the granite problem, which enables a limitation and clarification of the discussions.

I shall try to be as objective as he has been, my aim being, like his, to extend our insight as far as possible. I shall also endeavor, as regards my concepts, to define what I consider as a scientific certainty and what only an hypothesis, which, I think, is useful.

In my opinion, four questions should be raised:

1. Are there any granites formed by replacement in the solid? It seems useless to discuss this question, for the answer, which was negative when I expressed my theories some twenty years ago, is now universally positive.

2. Are there granites and granites, some formed by replacement in situ, some by crystallization of magmas, and some resulting from rheomorphism or diapirism?

3. What is the mechanism of granitization, diffusion in a stationary medium or transport of substances by circulation of hot solutions responsible also for migmatization and metamorphism?

4. What is the reason for the migration of matter?

PRELIMINARY CONSIDERATIONS

Before approaching the problem, it seems useful to sum up briefly the experimentally established facts, as well as what one is therefore entitled or

not to assert. (This is all the more necessary as no one has made the synthesis of granite, either by extremely slow cooling of a magma or by reaction in a solid.) (1) It has been shown that water vapor in particular facilitates and increases the speed of synthesis of minerals, but practically instantaneous syntheses of minerals by reactions between solids alone have also been achieved, for instance forsterite and enstatite by Sabatier (1950). It has also been shown that an addition of water, of 6 to 8 percent in weight, lowers the melting point of granite to approximately 650°C. under corresponding pressure of water vapor. Water does not seem to have any action on the melting point of basic rocks. (2) Certain experiments on surface diffusion (grain boundary diffusions) have shown relatively high speeds (Ramberg, 1952, and others), which are sufficient to explain the geological facts. (3) Much has been written on the considerable slowness of lattice diffusion. But in fact, experiments published are fragmentary and concern very particular cases only. The difficulty of measuring makes them often imprecise and does not allow, to my mind, extrapolation to the considerable geological times. I have already written on this subject (Perrin, 1953) and shown for instance that oxidation of copper-zinc alloys has taken place according to five different modes of diffusion of oxygen and that the experiment carried out at a temperature as low as 350°, which showed the smallest difference in oxygen concentrations, has given the highest diffusion speeds. For all that, calculations and extrapolations of authors are based on the assertion that diffusion speeds are governed solely by the difference in extreme concentrations, which gives an average distance of diffusion x proportional to $\sqrt{t}$. I have recently presented a paper to the French Academy of Sciences mentioning two instances of diffusion in metals which show that, in both cases where there has been precipitation of new crystals by chemical reactions, the above assertion is erroneous. The existence of a chemical motor may mislead all arguments based on variations in concentration and applying Ficks' laws; Ramberg (1952) recognizes that such laws have but a limited value. Therefore, despite Verhoogen's conclusions (1952) based on a dry electrolysis of sodium chloride through a lamina of quartz and the equation $x = \sqrt{2Dt}$, I do not "take small comfort in this work." I agree with Walton that experimentation in this matter is still in its early stages. (4) Very valuable data have been given by Bowen and Tuttle (1950) on diagrams of feldspars: thorough miscibility in the solid state of potash feldspars and soda feldspars during solidification, then immiscibility at lower temperatures, with equilibrium at each temperature between two feldspars, one richer in K, the other richer in Na. (5) There exist in lavas and plutonic rocks two different forms, high temperature and low temperature, of potash feldspar and of albite, the transition from the low temperature form to the high temperature form being attained when the temperature remains sufficiently high; so far, however, the reciprocal transition has not been observed. Moreover, all syntheses in the presence of water vapor, even at as low a temperature as 250°, give the high temperature form of the albite (Tuttle and Bowen, 1950).

DISCUSSION

We can now deal with our problem, having in mind that in the present state of our knowledge observation should be our major guide, and then, starting from such observation, the logical deductions based on positive scientific knowledge and not on subjective impressions. If the conclusions based on such definite scientific arguments are in contradiction to more or less hypothetical points of view, the former should take the lead. I shall therefore begin by summing up briefly the essential observations and arguments that led me in 1935 to the concept of the genesis of granite by replacement in the solid.

I had noted a fundamental fact, observed by many others before me, in particular by such eminent French authors as Auguste Michel Levy, Ch. Barrois, Ch. Lacroix, and by many others since then, namely, the development in the country rock (mica schists, for instance) near the granite contact, of feldspar crystals thoroughly identical with those of the granite in all their features: shape, size, analysis, color, inclusion of relics of biotite or hornblende, etc. Whoever has actually studied crystallization phenomena is aware of the extreme sensitivity of crystalline forms to all the conditions of the medium in which crystals develop. The line of reasoning should be as follows: There is practically no probability for feldspar crystals, identical up to their tiniest peculiarities, to have generated and developed a few centimeters apart according to processes as different as, on the one hand, crystallization of a molten magma and, on the other hand, crystallization in an unquestionably solid medium of different texture and composition; this is almost a scientific certainty. One should conclude therefore that the granite feldspars have been generated in the solid (some larger feldspar crystals sometimes bridge over the edges of the two rocks). Many physicochemists to whom I have outlined this line of reasoning have, without any hesitation, confirmed unreservedly my point of view. To invoke convergences or soaking of the enclosing rock would in no way modify the conclusion. H. H. Read's (1944) arguments are practically identical.

Moreover, it often happens that not only one but several of the granite crystals, and even whole areas of granite, are formed in the country rock (Perrin, 1954b, pl. 2). The same phenomenon of feldspathization is extremely frequent in mesocratic inclusions (or inclusions of mica schists) in granite that have also remained solid, since they melt solely at much higher temperatures than the temperatures admittedly necessary for granitic magmas. On the strength of these observations in batholiths having an eruptive character, sending veins and dikes in the country rock, I have given preference to the scientific certainty over the subjective impression, and have written with Roubault (Perrin and Roubault, 1939) that these dikes must have been formed by replacement, giving proof thereof in some cases. Now, the eruptive character is not considered as a proof of injection of liquids, since such authors as G. G. Goodspeed, B. C. King, R. Higazy, Phemister, Barth, Roubault, and myself have given the proof of formation by replacement of dikes and veins for pegmatites and aplites as well. Feldspathization is very common and can be seen in many granites and on pavements or house fronts

throughout the world; therefore the formation of granite by replacement in the solid is, to say the least, very frequent. Some authors have objected that while this is true of the fringe of batholiths the heart at least might be magmatic. To say nothing of feldspathization of inclusions often found in the very heart of bodies, I would say again: There is practically no scientific probability for strictly identical granite portions to have generated, one on the rim by replacement in the solid, the other in the heart by crystallization from a molten magma, these two processes being entirely different.

There are other facts in addition to this basis argument: (a) observation of digestion by the granite of dikes which, in other places, cut it sharply (Perrin, 1935), namely, the relict dikes of Goodspeed (1955); (b) formation by replacement of dikes and apophyses; (c) proof by Roubault (1939) and myself that in many granites and sometimes even deep down (Pyrenees, Kabylla de Collo) crystals had partially replaced others in the solid; this is what we have called corrosion between crystals, which corresponds partly to what American authors have called the "crystalloblastic structure"; (d) work of Bowen and Tuttle (1950; Tuttle and Bowen, 1950) on diagrams of feldspars which has led these authors to the hypothesis of a complete recrystallization of these feldspars at a low temperature in the solid—this seems, at the least, to confirm our former statements, namely, that the granitic structure is characteristic of crystallization in the solid; (e) the fact that in the great majority of granites, the feldspars of the low temperature forms (and also the quartz) are identical with those of metamorphic rocks generated by replacement and different from those of lavas. There again, it is most likely that the genesis mechanism is the same for gneisses and granites and different for lavas. D. L. Reynolds (1952) has rightly emphasized this point in favor of transformist conclusions. Indeed, it seems to me unlike the logical spirit to find minerals similar in granites and gneisses and different in lavas and to conclude that the genesis is the same for lavas and granites and different for gneisses. Tuttle and Keith have recently described (1953) quartzes and feldspars in Skye granites, rather on the higher temperature side, and has concluded to their magmatic origin. This conclusion is quite possible if quartzes and feldspars alone are considered,[1] but not necessary, as I see no reason now why granitization could not take place at a temperature such as 700°.

I shall briefly deal with another point which Walton seems to consider as natural and logical in the magmatic process: assimilation of inclusions. The word "assimilation" is indefinite; study of these inclusions often shows that inclusions lying side by side, or even portions of one inclusion, have been transformed irregularly (Perrin and Roubault, 1939, pls. 1 and 2). There cannot have been simple dissolution, like that of a lump of sugar in water, as the analysis would then show a mixture of the analyses of the granite and of the initial inclusions, which is not the case. Examination and analyses often show, for basic inclusions, that they have become richer in Si and alkalies

[1] B. C. King (1954) has recently concluded that the granite of the Creag Strollamus Area of Skye, similar to the other granites of the island, has been formed by replacement of Torridonian sandstone.

and poorer in Mg and Fe, and this until the inclusion has become almost exactly granite-like (Perrin, 1954b, pl. 1-A and B).

In cases where such observations have been made, where is the scientific probability? Isn't it natural to think that the positive mechanism, as illustrated in the field, of diffusions in two directions, in the solid inclusion, which has led to a body practically identical with granite, has reached its final completion as granite? Indeed this seems to me certain since the feldspars of the granite are identical with those of the inclusion. The process of "assimilation" should be studied in each case, and a broad term does not seem to me to be considered as sufficient.

In the light of the above, I can now deal with the questions which I had raised at the beginning of this paper:

ARE THERE GRANITES AND GRANITES?

I shall first set forth the principle that crystallization of granites is very peculiar and even abnormal for a direct crystallization from a liquid containing water. It is abnormal and commonly occurs that the first crystals that have settled, hornblende or biotite, should contain water, whereas those that have followed, plagioclases or alkaline feldspars, should be anhydrous and that, finally, the water should concentrate with the silica which, although a constituent in excess, is the last one to settle and finally molds all the other crystals and loses its water at the same time. Cases where biotite has been the first to crystallize, then the plagioclases which are almost without any potash, the settlement of potash being resumed in the potash feldspars, are also abnormal. I do not know of any such peculiar diagrams of solidification, nor do my friends that specialize in such diagrams and with whom I have raised the question.

I must say that the structure of granites is really very peculiar, and following my line of reasoning: The probability for formation in some cases of such peculiar structures, by simple crystallization, from a liquid, and in other cases by replacement in the solid is, a priori, very small. In this case it is not a scientific certainty but only a very small probability. This is the argument on which I base my extreme transformist point of view, which may be summed up as follows: In view of this high improbability, I shall admit that a particular granite, having the normal structure of granite, is magmatic, in the proper meaning of the word, only if convincing facts compel me to recognize that there is no other possible explanation for its genesis. This is not for me a case of "personal psychology," it is a question of logic. On the other hand, I quite agree with the possible subsequent granitization of lavas (it is even certain in some cases I know of, rhyolites in particular): it would be preposterous to state the contrary but it does not seem obvious, a priori, that such granitization of rhyolites has not been accompanied by diffusion, all the more as rhyolites are generally richer in silica than granites.

Therefore, the problem consists in ascertaining whether there are cases where it is impossible to consider another hypothesis than the purely magmatic granite. A very good basis to proceed with this examination is Walton's article:

Room problem.—The room problem is the objection generally raised by the transformists to the magmatists, but Walton turns the objection around to the transformists in the case where there has been deformation of the country rock and where no member of metasedimentary terrains is missing. It is quite certain that intrusion of magma may create deformations in the terrains as shown in the interesting articles of Noble (1952) and Hunt (1954) cited by Walton, but, to my mind, nothing seems to demonstrate that deformation is particular to magmas; even without putting forward a tectonic diapir of rheomorphism, I do not see why replacement in the solid by chemical exchanges is not capable of causing, in certain cases, changes in volume and deformations. This has been proved experimentally.

Also, it is not abnormal that when granitization involves a change in volume it occurs preferably in the anticlines. The case is known for migmatization; see for example Guitard (1953).

Neither do I see the preposterousness of the hypothesis that the granites of the Adirondack pyroxene-quartz syenite series have granitized terrains underlying the Greenville sequence, even if such terrains have not been noticed anywhere else; this series certainly overlaid other rocks, and the fact that they have not been noticed is not a proof that they do not exist. In Algeria, in Kabylla de Collo (Roubault, 1935), a complete, scarcely metamorphic Eocene is plicated and floats on a granitic batholith; farther south, it overlies unconformably mica schists and gneiss. One is entitled to think that these are the ones that have been granitized farther north during the Tertiary, but if the southern part was not visible, one could nevertheless not state positively that the granite of Kabylla is magmatic because nothing of the Eocene is missing. Indeed, the room problem would create a ticklish situation in the magmatist hypothesis in the case of this batholith of considerable thickness, the section of which can be seen from 12 kilometers, and which splays downwards.

I shall mention but this one instance among others, for my statements have never been based on the room problem, but I do not believe either that the negative room problem may constitute an important objection and still less a proof.

Disharmonious granites.—This term, cleverly chosen by Walton, contains in itself Walton's objection and conclusion. A similar idea has been put forward by H. H. Read (1952) and has led him to conclude against granitization "in situ" of Cape Pluton, another argument being the strong deformation in some localities of the Malmsbury Series; he ascribes the disharmony and deformation to rheomorphism.

I am not quite clear, on reading Walton's paper (1955), as to the cases in which he concludes to magmatism and those in which he concludes to diapirism or rheomorphism. Walton writes that the metamorphists have substituted a heat problem for a room problem. It seems to me that his argument is summed up when he writes (p. 9): "The contact metamorphic aureole in which minerals such as clays, stable at surface temperatures, are recrystallized into minerals stable at higher temperature, proves that the disharmonious granite mass represents a highly localized source of heat in a low temperature

environment" and, on the other hand, by the idea that this source of heat can have been brought only "bluntly" (p. 10) by an intrusion of hot mobile rock material, or still better of "hot magma." At first sight, the argument is very striking, as was the eruptive appearance a few years ago. But, in my opinion, it involves two hypotheses:

(1) The contact metamorphic aureole has been brought to a much higher temperature than the unchanged part of these terrains, as heat by itself is sufficient to cause contact metamorphism. (2) Granitization implies a pre-existing hot temperature and is not by itself a source of heat. To my mind and in the present state of our knowledge, these two hypotheses are not proved, and observation should be the leading factor to conclusions.

In France, despite the relatively small size of its territory, disharmonious granites are not uncommon, and some of them have in fact been made the object of fine studies by the great authors of the French school to whom Read, Backlund, etc., recently paid a just tribute. I shall mention in particular the granites of Huelgoat in Brittany (Ch. Barrois), of Quérigut in the Pyrenees (Ch. Lacroix) where the granite intersects "à l'emportepièce" without disturbance, Paleozoic sedimentary strata: shale, sandstone, and limestone. In such cases, part of the sedimentary series is missing, but their uninterrupted or interrupted prolongation can be traced in the granitic mass of some of them; the sandstones become quartzites, slightly metamorphic; the shales and limestones undergo a stronger transformation, the beds of limestone extending along the strike over several kilometers (Quérigut), either as metamorphic limestone or as basic rocks: norite, hornblendite, and even peridotite. Similar observations have been made in the Champ de Feu batholith (Vosges) by H. Bückling, etc.

Proofs of replacement in situ are many, including for some of them feldspathization, transformation of inclusions. At Flamanville (Aug. Michel Levy), where feldspathization is intense, parts of strata are missing despite strong deformation of these strata around the granite. In all the above-mentioned cases, a contact aureole is to be found in a low-grade metamorphism rock. What, to my mind, should be concluded, except that there exist decidedly disharmonious granites whose granitization is however certain? The criterion of disharmony does not therefore seem sufficient in itself; along the same lines, the observations mentioned do not sem to back up the hypotheses expressed in support of the heat problem by Walton. Our former authors mentioned above would ascribe contact metamorphism not to heat alone but to mineralizers, represented to their eyes by the presence of hydrated or fluoborated minerals. The fact that heat is not the only factor involved is shown in the Kabylla de Collo. Despite the large size of the batholith, the Eocene clays overlying it have been but slightly metamorphosed through a small thickness, producing particularly chlorite, a few small biotite crystals, and skeleton andalusite. It seems difficult to admit that important variations in temperature may have occurred a few meters away. But in view of the importance of the problem, it seems useful to bring still further evidence of what I state: Hüttenlocher (1947) has observed on the southern ridge of the Aar massif (Switzerland) granitization of a Permian conglomerate known to be intact

not far away and overlain by Trias and Lias, with very low-grade metamorphism: mostly sericite. In the case of a conglomerate, I think we have a right to speak of "granitization." Peter Misch (1949) has made a remarkable observation and description of the static granitization in the Sheku area (China) of the "upper red beds" which show epizonal metamorphism. He writes: "The new granitized sediments enclosing the granite bodies do not show thermal metamorphism of regional extent," etc., etc. The proofs of granitization furnished by him cannot be denied. Similar instances exist for migmatization hardly separable from granitization: migmatization of the Permian conglomerate of the Vanoise (French Alps), of the Primary schists of the Pyrenees, etc. As shown by Jung and Rocques (1952), the front of migmatites reaches a more or less high level in the metamorphic series according to locality, up to the epizone.

In all these cases, it does not seem possible that the strata that have remained at a low-grade metamorphism at some distance have been brought to a much lower temperature than that of the granitized or recrystallized parts. In these temperature ranges, certain chemical exchanges are probably necessary to achieve high-grade metamorphism.

I have observed (Perrin, 1954a) in metamorphic series, the intercalation of green schists with chlorite and sericite between amphibolitic beds, and other authors have also.

In view of this "disharmonious granitization" and of the fact, which seems very likely, that granitization requires a minimum temperature, one may wonder what is the origin of the corresponding heat. Here I too am expressing hypotheses. The only point which seems scientifically certain is that granitization is involved in a general process of transformation of the lithosphere, an "equilibriopetal process" as Ramberg calls it. Such a process is necessarily governed by the tendency to lower the level of free energy; such diminution of free energy results necessarily in an emission of heat or development of mechanical energy, also resulting finally in an evolution of heat, or both, simultaneously.

Two hypotheses are possible if we want to go further: a) the evolution of heat has nothing to do with granitization, and such granitization is only a consequence thereof; b) granitization itself (and probably also metamorphism) contributes to the evolution of heat and is exothermic. The latter is Ramberg's hypothesis and mine.

With respect to the first hypothesis, the supply of heat by circulating hot solutions considered by Peter Misch and other authors solves the heat problem, but it does not seem that the geological observations support this hypothesis of circulations, as their existence should lead to the presence of very important basic fronts. Other origins may be set forth, but I fail to see which, apart from the mysterious concentration of radioactive elements. On the other hand, the exothermicity of granitization does not seem unlikely, but the contrary, since Ramberg has shown that the tendency to the lowest level of free energy requires concentration of the alkalies in the tecto-silicates and of the ferromagnesians in the metasilicates and orthosilicates, which corresponds to the phenomenon of granitization. Yet lowering of the level of free energy

implies evolution of heat, and if Ramberg's conclusions are correct, granitization should therefore be normally exothermic. To my mind, this is not inconsistent with the fact that the weathering of feldspars is exothermic, as the chemical reactions are entirely different in the two cases.

If we follow this hypothesis of exothermic granitization—and so far, I see no convincing evidence that it is erroneous—I think we can find there a reasonable, complete or partial explanation of the heat problem. Variation in volume may also bring about mechanical deformation, just as any chemical process, but the possibility of this deformation is a function of the thickness and external shape of the terrains overlying the interested area; the distribution of the energy developed by the diminution of free energy between evolution of heat on the spot and deformation is therefore governed by the general conditions of the region; as a comparison, in a combustion engine the temperature would be much higher in the chamber if the piston were blocked than if it transmitted mechanical energy. Such is the very simple basis of the hypothesis, I say of the "hypothesis," which I outlined concerning the origin of volcanism and which seems to have shocked Walton. I am sorry that the lack of space prevented me from explaining it, and especially that I did not make it sufficiently clear, when I spoke of impossible plastic deformation, that I referred to deformation of the whole of the overlying terrains, involving formation of superficial relief, and not only to deformation of immediately overlying terrains, which is not the same thing.

Experiments of underground explosions show indeed that there may be a considerable plastic deformation around the cavity resulting from the explosion, without any consequential effects on the outer relief. It is not therefore obvious that plastic deformations of deep strata are always accompanied by formation of important external relief. Highly plicated and plastically deformed strata under more recent beds that have remained practically horizontal and undeformed may be seen in the French Alps. P. Pruvost has observed similar striking facts in the coal formations of northern France.

Therefore, I think that the existence of considerable plastic deformations in the deep-seated strata is not inconsistent with my hypothesis on the origin of volcanism, which is pretty much in line with that of Ramberg on the formation of rhyolitic streaks.

In concluding this subject, I hope that the reader will understand why, in view of the existence of disharmonious granites certainly formed by granitization, it does not seem to me that "disharmony" is a sufficient criterion in itself for magmatic intrusion or diapirism or rheomorphism, while I readily accept the fact of intrusion of diorite porphyry in the Henry Mountain following Hunt's elaborate descriptions. I think that each case should be made the object of a detailed study and each point should be carefully considered, in particular as regards the development of feldspars, existence and evolution of xenoliths, septa, high temperature or low temperature character of the feldspars, the nature and the number of alkali feldspars (Bowen-Tuttle diagram), the crystalloblastic or non-crystalloblastic structure, etc.

Crystalloblastic structure.—I have just said: the crystalloblastic structure; Walton accounts for it by the so-called "endomagmatic solution" and re-

crystallization (Tuttle, 1952). It seems to me that Tuttle has adopted recrystallization, resulting from a general metamorphism, i.e. an "autometamorphism," specially to explain by exsolution the coexistence in a granite of albite and orthoclase crystals, which coexistence is inconsistent with the feldspar diagrams; he does not seem to have extended this autometamorphism to the general explanation of crystalloblastic structure and to the so peculiar and common forms of crystal corrosion by other crystals implying diffusions on another scale than the crystal scale. Ermansdörffer expresses this hypothesis of autometamorphism by endomagmatic solutions (1950). In the line of reasoning of scientific probability, I would say: such crystalloblastic structure or corrosion between crystals seems particularly common in metamorphic rocks that have certainly been formed by replacement: gneiss, migmatites. In granitization, they are often particularly noticeable on the fringe or in the inclusions in places where granitization is still incomplete. Isn't it therefore a strong point in favor of an origin by replacement when they are found in disharmonious granites, for instance. Besides, the assumption of autometamorphism, whatever origin is claimed, amounts in fact to superadding a replacement in the solid state to the magmatic origin; the characteristic crystals of this new structure being very often feldspars, a new feldspathization must be assumed, which latter feldspathization cannot be "blunt." Why, therefore, under the protracted action of the endomagmatic solutions, according to Walton's ideas on the influence of heat, should the enclosing low-grade metamorphism rocks have remained low grade as, among other cases, in Kabylla de Collo where Roubault has observed (1939) very fine corrosions of crystals by others in the granite? I think we may sum up by saying that the crystalloblastic structure is characteristic of replacement. This is actually the useful idea for the observer.

Observation of feldspars is also important. I fail to be convinced of the accuracy of Tuttle's hypothesis, according to which the exsolution of mixed K-Al feldspars can, under the influence of metamorphism, go as far as a complete separation into an orthoclase crystal and a crystal rich in albite. I do not mean, for obvious reasons, that I do not consider the possibility of diffusions in the solid—but this division into two separate crystals, often not edge to edge, of a crystal, the volume of which is almost equal to the total amount of the volumes of the two crystals, is really peculiar, and no other explanation seems possible but a total recrystallization of the rock and not a simple exsolution, such as that which has occurred in the microperthites that are often to be found in granites. Nor can I understand why the frequent inclusions of relics of biotite, hornblende or quartz, would have been specially enclosed in orthoclases alone during a simple process of recrystallization. And what about the cases where three and even four types of feldspars, some of them zoned, are to be found? Tuttle's idea of reconciling magmatic origin with the feldspar diagrams and observations is very ingenious, but it seems to me that the probability, in the case of "disharmony" between the observations and the Bowen-Tuttle diagram, is in favor of replacement. Such disharmony is in fact often to be found in obvious cases of granitization.

Indeed, the strongest and most intriguing impressions in favor of a magmatic origin of the granites, whether disharmonious or not, are the eruptive character, in particular dikes and apophyses, but the many and convincing proofs of such appearances by replacement have removed my perplexity in this respect.

I realize, however, that many authors are still oriented toward the concept of a magmatic origin, or at least rheomorphic, when they observe a granite which recuts with sharp borders strata and especially a series of different strata, in particular when feldspathization is low or inexistent.

The sharp border does not seem to me a criterion in itself (nor is the recutting of different strata) since it exists in definite cases of replacement, involving for instance important development in the country rock of feldspars identical with those of the granite or whole granitic areas (Perrin and Roubault, 1939, pl. 1, fig. 5, and pl. 2, fig. 2; Perrin, 1954b, pl. 2-B), and other criteria such as the prolongation of certain strata in the granite. On the other hand, I do not see why the complete absence of feldspathization will establish a definite proof (it is indeed the case for the granite of the Kabylla de Collo). The reasons that prompt me to express this opinion are as follows: (1) Granites are to be found where feldspathization occurs in very localized places only and not generally. (2) It happens that out of two inclusions of a similar rock, side by side, one is feldspathized while the other is not; I know that in such cases authors have surmised that one inclusion comes from a deeper region and the other from a superficial region, in accordance with the magmatic concept, but I have often noticed this unevenness of feldspathization in one single inclusion (Perrin and Roubault, 1939, pl. 1, figs. 7-14).[2] Besides, since the granite feldspars are identical with those that have developed in a solid rock, the conclusion, according to the above line of reasoning, is that these feldspars have originated in the solid; no matter how many feldspars have been observed. (3) There are no sharper borders, not accompanied by feldspathization, than those of certain aplite dikes, certainly formed by replacement, as shown by G. C. Goodspeed, B. C. King, and ourselves. The sharp border is therefore not inconsistent with replacement.

I have also made the following frequent observation: granites of small grain size, occurring in some cases with what is sometimes called the "new granites" that recut in particular the "old granites," seem to have feldspathized the country rock to a much lesser degree than the coarse-grained granites and particularly the porphyritic granites; they are often also more homogeneous. And yet proofs of granitization were certain in those I have observed, including limited feldspathization, particularly of enclaves. Such granites are generally more acid and alkaline than the old granites that they recut, their crystals more euhedral, but they often contain at the same time a potassic feldspar and albite or a plagioclase close to albite. It seems particularly difficult to admit Tuttle's hypothesis of exsolution in this case, since metamorphism would have been the source of a recrystallization that would have

[2] Needless to say, the reasons for such unevenness, which commonly occurs in terrains of magmatic stoping in particular, are not presently known.

converted only the new granites, exclusive of the old granites that are by their side.

I am inclined to think that the difference in behavior concerning the grain size, homogeneity, and feldspathization results from differential speed of the propagation front of granitization, but of course I must say this is just an hypothesis. I readily admit that the sharp border conveys the impression of intrusion; the same applies to granite, aplite or pegmatite dikes. This does not preclude, however, that in many corresponding cases definite proofs of formation by replacement exist. I think it is reasonable to bear this idea in mind and to set aside the sensorial impressions.

Let us now consider the relatively rare cases of so-called displaced inclusions, i.e. with discordant schistosities, suggestive of displacement by a liquid. I have endeavored to study most carefully some cases and am now convinced that replacement had nevertheless taken place in this peculiar case (Perrin and Roubault, 1952). In order to understand the possibility of the presence of inclusions with transgressive schistosity in cases of granitization, one should examine figure 1 of Cogné (1951), which is reproduced here, among many other instances; if we consider a further partial granitization where inclusions are still to be found, we come to figure 2 which needs no further comments. I must confess that there are certain exceptional cases of displaced enclaves, described by authors who have given sketches thereof, that still puzzle me. However, in view of the abundance of compelling proofs of granitization in some of these cases, I am inclined to think that explanations for these appearances, consistent with granitization, must exist. Unfortunately, it is difficult to see them without very close personal observation in the field. Roubault and I will shortly publish a paper on the subject of displaced enclaves in which we shall describe precise observations and shall furthermore set forth generally the various possible explanations relating to the granitization hypothesis, such as (a) development of a new schistosity in the enclaves, which is a well-known fact, (b) granitization of lavas containing inclusions, or grinding zones, or mixtures of strata of various rocks, resulting from more or less plastic deformations involved by the changes in volume that may accompany metamorphism and granitization. Fine instances of such mixtures at granodiorite contacts are reproduced by W. S. Pitcher (1953, figs. 7 and 8). If we imagine the aspect that further extension of granitization could have given to these zones of mixtures, we realize that such a granitization in the solid is not inconsistent with the existence of displaced inclusions, as displacement may have occurred prior to granitization. The essential purpose of our forthcoming paper is to furnish elements of appreciation to the observers regarding this problem of displaced inclusions which, I would repeat, is rather uncommon, while the presence of inclusions with parallel schistosity is very common.

Diapirism and rheomorphism.—Of course, the existence of "displaced inclusions" is easily consistent with granitization if we admit rheomorphism, at least partial, or diapirism. It would therefore be very convenient for me to admit unrestrictedly these mechanisms, but I must confess that without denying a priori their possibility I cannot make up my mind to follow the

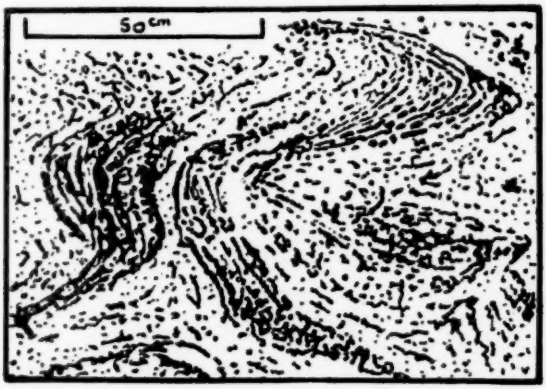

Fig. 1. Migmatite of the Rance Valley, Brittany, France.

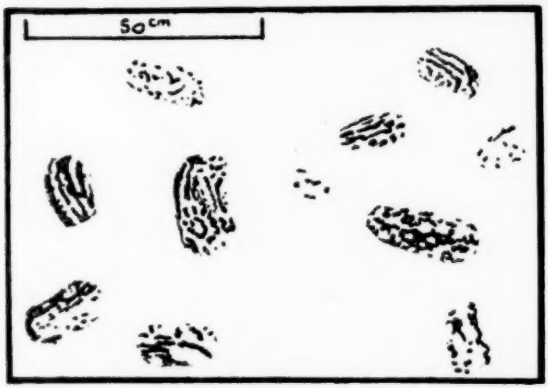

Fig. 2. Appearance of displaced inclusions that might result from progressive granitization of the migmatite in figure 1.

example of other metamorphists who admit them and especially those who introduced them into geological thinking, such as Wegmann and Backlund. The reasons that prevent me now from doing so are as follows:

(1) What does not seem obvious to me, in particular as regards rheomorphism as described by metamorphist authors is, in the first place, the partial melting which implies—to allow real possible mobility—the mysterious introduction of a relatively important amount of water into an already granitized rock. (2) Also, and this is all the more true in the magmatist hypothesis, the removal of this amount of water should have normally resulted in a substantial decrease in volume and a corresponding subsidence of the granite, no trace of which is to be found. I would even say it is the contrary, since rheomorphism is invoked particularly in the doming cases. (3) Finally, according to Bowen and Tuttle's work, even at a low temperature, the syntheses of plagioclases have always given high temperature forms, and rheomorphism

should therefore have led to such forms of the new feldspars while, mineralogically, it does not seem that such a difference has been indicated between the rocks that are considered as rheomorphic and the others.

Let us now consider diapirism. The salt domes exist and so do tectonic diapirs of Triassic gypsum; it is also true, although there are but few cases, that shales or marbles (Grenville series) have penetrated the overlying terrains. This is accounted for by the difference in density in the first case, but it does not seem that such explanation can be applied to the second case. However, from the standpoint of one who is primarily a metallurgist, I do not wonder that some bodies can punch other bodies under the influence of mechanical stresses, particularly if fissures open. I am used to cold-working. Balk attributes the mobility of granites to the easy deformation and recrystallization of the quartz, while Walton ascribes it to a partial remelting which, according to him, may take place at temperatures as low as 400°, which seems surprising. Why is the privilege of diapirism and partial remelting particular to granite rather than to micaceous quartzites, arkoses, gneisses, etc.?

To explain an ascension of the granites without partial remelting by difference in density, Ramberg (1952) applies the law of Stokes to a sphere of granite, 10 kilometers in diameter, moving in a medium having a viscosity of 10^{22} poises, but the law of Stokes implies a spherical shape which enables the liquid to flow freely beneath the sphere. Can granitic batholiths which usually widen downward be compared with spheres, and would not their ascension have required much more considerable mechanical stresses of deformation on the overlying rocks than the ascension of a sphere in the same environment? Observation shows that, despite a very great difference in density, big masses of chromite or pyrite or iron ore, etc., have not sunk into the underlying strata, even when they overlie granites or pegmatites. It is nevertheless a fact, but in the opposite direction, that, according to the law of Stokes, the speed of ascension is proportional to the square of the diameter for a sphere, which would therefore make easier the ascension or the sinking of larger masses.

Further, as a result of their shape, would not these batholiths have carried away in their ascension strips of strata formerly in contact with them? Read (1952) thinks that the rise of the Cape pluton is due to diapirism because, instead of being in contact with what he considers to be its normal environment, migmatites and catazone terrain, it reaches low-grade metamorphic strata. But if I try on the map to reconstitute the section of this very large plutonic batholith, it seems difficult to understand how the said high-grade metamorphism strata have remained quite deep and why no strip has been carried upward, to be found above the batholiths in contact with the Malsbury series. The same problem arises for the Kabylla de Collo, etc. I can hardly believe that the separation has always occurred just at the contact of the granite, whatever the irregularity of its surface, as is the case for liquids in contact with a sphere.

In support of rheomorphism or diapirism, the arguments which are or may be set forth seem to be essentially the following: (1) the sharp borders,

(2) the fact that granites are disharmonious, specially in the practically total lack of contact metamorphism, (3) the presence of displaced inclusions, (4) the fact of flow structures, as Goodspeed has indicated in his interesting paper on the "rheomorphic dikes."

I have stated why in the present state of my knowledge the first three categories of facts seem consistent with granitization "in situ."

It does not seem either that flow structure, which can be observed in a number of rocks that have certainly remained in situ, in particular in metamorphic rocks, should be a definite proof of rheomorphism.

New observations seem to be desirable to allow a well-founded opinion.

WHAT IS THE MECHANISM OF GRANITIZATION?

There again, the only important question from the geological point of view is to find an answer to the alternative: transport of materials by circulating solutions or gases, or diffusions in a stationary medium, whether dry or wet, lattice or intergranular diffusion. (If I am inclined to favor lattice diffusion, it is because there again, failing any accurate scientific data, priority should be given to geological observation, which seems to be rather in favor of this mode of diffusion (Perrin, 1954c) without however any possibility of positive statement.)

I have dealt very briefly with this problem in my previous paper (1954b) and would sum up as follows: Since migmatization and granitization result most of the time from introduction of alkalies and removal of ferromagnesians, the movement of solutions brings about an expulsion upward of considerable quantities of Mg and Fe, and therefore results in large basic fronts. Observation being generally in disagreement with this idea, Fe and Mg have necessarily moved downward, which is consistent only with diffusions in a stationary medium.

Moreover, as recently emphasized by Read (1952), rocks such as quartzites and limestones often act as "barriers" to granitization, showing that granitization has stopped only for chemical reasons, because these strata are as pervious as the others to solutions (Perrin, 1954d). Diffusion in a stationary medium constitutes a certainty for me, since it is based on general geological observations which seem incontroversible.

WHAT IS THE ORIGIN OF MIGRATIONS OF SUBSTANCES?

I have expressed on this point, in the same article, what I consider to be just an hypothesis of an entirely thermodynamic nature, basing myself on Ramberg's conceptions; these migrations would result from the fact that the minimum level of free energy is reached when the alkalies concentrate in the tectosilicates and the ferromagnesians in the metasilicates and orthosilicates. This has nothing to do with the weight or size of the atoms to which, according to Walton, I particularly refer. I am no doubt partially responsible for this confusion because I wrote that the gravitational field of Ramberg was perhaps an additional factor, which only means that said gravitational field might favor migration without however causing it. But I realize that an idea which has become familiar to me because I am used to it may seem

foolhardy, to say the least, to other petrographers;[3] namely, that the physico-chemical equilibrium may tend to be attained at long distances between deep-seated minerals and more superficial minerals located on the front of granitization, through the channel of diffusion of traces of elements, through important thicknesses of strata, which are not interested any more in the equilibrium, just as if the crystals were edge to edge. If this very bold concept does not seem unreasonable to me, it is because I have witnessed similar experimental facts in metallurgy, on a quite different scale of course on account of the short times. Such reactions through channels of diffusion between non-contacting bodies are an experimental fact. In the progression of a front of decarburization of hard steels, annealed at 650° in the presence of vapor, the cementite Fe_3C decomposes to free its carbon, which diffuses as traces in the α-iron crystals of the part already decarburized, to combine with the oxygen of the vapor and to free hydrogen. In a brass oxidation process—Ehlers test (Perrin, 1953)—a similar phenomenon occurs inversely, the water vapor decomposes to release its oxygen which diffuses as traces in the copper crystals to form zinc oxide in the deeper layers. In both cases, when the reaction has started, it continues and the "front" progresses.

In petrography, (1) corrosion of crystals, the ones by the others, and (2) recrystallization of a rock with formation of new minerals, involve similar processes. Ramberg writes (1952, p. 91): "Some constituents are usually lacking in the closest surroundings and must be supplied from some distances, whereas other elements or molecular compounds are superfluous and likely to disappear from the site of universal growth." On a much larger scale, the same phenomenon is set in light, for instance, by dedolomitization of the Natal marbles, which contain large granite boulders (Du Toit, 1919; Hatch and Rastall, 1910). The dolomite located on the front of dedolomitization has released its magnesium or its magnesia, which have gone through strata sometimes many feet thick, already turned into pure calcite, to form magnesian silicates at the granite contact.

I hope these indications will help the reader to understand that my hypothesis is only the extrapolation on a large scale of the application of known scientific facts; once a current of ions is started by chemical reactions, it can proceed through on crystals or along the boundaries of crystals that have become passive, to achieve the decrease of the total free energy between minerals, the distance between which increases continuously without, however, involving gravity. But this is, I repeat, just an hypothesis. The only certainty for me is that the origin of migrations is an equilibriopetal process, involved in attainment of the lowest total level of free energy.

CONCLUSIONS

In fact, there are no conclusions. The readers and field observers should draw them themselves. I hope they will realize that my position as extreme

[3] It seems therefore that the following conceptions are less and less foolhardy: (1) long distance diffusions (Perrin, 1934), (2) concentration in the solid under the influence of metamorphism of traces of elements present in the pre-existing strata, to result in the formation of ore deposits, such as cassiterite, wolframite, sulphides, magnetite, ilmenite, chromite (Perrin, 1934). Such conceptions are now set forth by many authors for particular cases of ore deposits or in a broader form—e.g. Newhouse, Holmes, Rosenqvist, Ramberg, Sullivan, and the recent paper of De Vore (1955)—in a much more precise theoretical scientific form than I had formerly done.

transformist is neither a fancy nor a blustering attitude. My position is dictated by a conviction resting on both my personal observations and those of other authors, such as Bowen and Tuttle, that the granitic structure is characteristic of crystallization in the solid. This deep belief has prompted me to try and find the explanation, in the frame of granitization, of facts which at first sight seem to be in contradiction with replacement in situ in particular for the intrusive appearance and the formation of dikes. I still proceed in the same way with regard to much more uncommon facts; the reader may think that perhaps I go too far in that direction. It may be; time will show it, and I will not hesitate to change my attitude in the presence of unquestionably convincing facts or proof of scientific errors on my part. In any case, my inferences are essentially based on observations in the field.

I hope that, like Walton, but not always in the same direction, I have brought elements which will enable the readers to draw for themselves their conclusions as regards the granitic bodies which they have observed or will observe with the greatest care. As far as I am concerned, I shall only say that I am most thankful to Walton to have summed up the present state of the granite problems with such remarkable clarity and I am pleased to express my tribute of praise. Partial divergence of opinions does not exclude high esteem.

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ABSOLUTE AGES OF THE ARCHAEAN OROGENIC CYCLES OF INDIA

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ABSTRACT. Correlation within the Archaean rocks of India has been difficult and, without the aid of radioactive age data, not very satisfactory. The available age data pertaining to the Archaean obtained by the Pb-U-Th, alpha-helium, and Rb-Sr methods are presented cycle-wise, and the degree of dependability of each determination is given. The Eastern Ghats orogenic cycle (1625 ± 75 M.Y.) is older than the Satpura (955 ± 40 M.Y.) and Delhi cycles (735 ± 5 M.Y.), and younger than the Dharwar cycle (2300 ± 100 M.Y.)—a succession which is fully consistent with the structural evidence. Recent advances in the field of measurement of geologic time have thus facilitated the bringing together of two distinct, but nevertheless mutually related, approaches; namely, the correlation of rock formations and the dating of orogenic cycles.

PREVIOUS NOMENCLATURE AND CORRELATIONS

The term "Archaean" was originally proposed by Dana (1872, p. 253) to designate all the Precambrian formations. Subsequently, in the United States, the Precambrian formations were separated into two systems—an upper Algonkian system, which includes undoubted original sediments lying below the base of the Cambrian, and a lower Archaean system, which consists of granitic, gneissic, and schistose rocks, among which are seldom found beds of quartzite, limestone, or any other indubitable clastics. These two systems are no longer generally recognized as time units in the United States, however.

In India, the formations below the Eparchaean unconformity (the unconformity at the base of the Cuddapah system and its equivalents) were included in the Archaean. It must, however, be admitted that, at present, there is no strict definition for the term Eparchaean unconformity, particularly as the Cuddapah system cannot be correlated with formations in other parts of India "officially" regarded as its equivalents (personal communication from Professor Holmes). The so-called Lower Transition System consisting of certain sedimentary rocks, and mixtures of sedimentary and igneous rocks was included within the Archaean. These rocks, which occur in compressed and partly buried synclinoria in South India, were grouped in the Dharwar system of Bruce Foote (1886). The term Dharwar was later extended to similar formations in other parts of India and has been widely used to designate the schistose Archaean rocks older than the Eparchaean unconformity. Such a wide usage of the term seems unfortunate, firstly because it tends to confuse the Archaean chronological succession and secondly because, like the term "Laurentian" in North America, it is incorrectly used to designate rock formations that are widely separated geographically and chronologically. On these grounds, Holmes (1949) expressed himself strongly against the use of the term "Dharwar" for the rocks of the Satpura and Eastern Ghats belts. It has been very correctly stated that "the term has become so well entrenched in Indian geological nomenclature that it is scarcely possible to discard it" (Krishnan, 1949, p. 94-95). The term "Dharwar" will have to be retained, but in the interests of clarity of stratigraphic nomenclature, it is better to restrict it to the type area in South India.

Archaean rocks occupy about two-thirds of Peninsular India. "They stretch continuously from Cape Comorin to the Central Provinces and Bihar and apparently continue underneath the Ganges alluvium into the Assam plateau; the Mysore area is also presumably connected with that of Gujarat and Rajputana beneath the Deccan Traps" (Krishnan, 1949, p. 96). In Extra-peninsular India, Archaean rocks are found in the Lesser Himalayas.

Correlation of the Archaean formations of Peninsular India is much more difficult and complex than correlation of the higher sedimentary systems. For the latter, stratigraphic correlation is usually a comparatively simple job as, in most cases, at least one of the major criteria for stratigraphic correlation (lithology, stratigraphic superposition, and fossil content) is available. "These criteria are, however, either absent or comparatively of little help in the case of Precambrian formations, and especially of metamorphic complexes, for they are devoid of fossils, their lithology is transformed by metamorphism, and their stratigraphical relationships confused by intricate folding, disturbance, and dislocation" (Krishnan, 1949, p. 140-141). The cumulative effect of regional metamorphism, igneous contact action, magmatic stoping, assimilation, and hybridism has resulted in the production of a bewildering variety of petrological types with complex characters which must necessarily be difficult to unravel.

Fermor (1936) made the first systematic attempt to correlate the ancient schistose formations of the Peninsula. He (1936, p. 42) demarcated two regions in the Archaean rocks of the Peninsula—the non-charnockitic (including iron-ore provinces, manganese-ore marble provinces, and igneous provinces), and the charnockitic (also including iron-ore provinces and manganese-ore marble provinces, of normal type and garnetiferous type). The separation was based on the belief that the charnockitic region of Archaean rocks had witnessed a plutonic invasion of charnockite and at the same time had been subjected to a severer degree of metamorphism (hypo-metamorphism) than the non-charnockitic region. The validity of such a separation was later brought in question by two significant observations: (1) there is no clear evidence for the major fault separating the charnockitic and non-charnockitic regions postulated by Fermor (1936, p. 48-49), and (2) all the types of hypo-grade rocks enumerated as characteristic of the charnockitic region except khondalites and eclogites have been found in the Sausar series of the Central Provinces and therefore outside the charnockitic region (Pascoe, 1950, p. 70). The association of marbles, manganese ores, and iron ores which Fermor took up as a major criterion for purposes of correlation, was based on the assumption that at a certain period of Earth's history these special groups of sediments were formed.

AGE DATA

With the objective of dating the pegmatitic cycles of the Archaean structural provinces (Aravalli, Dharwar, Eastern Ghats, and Satpura), detailed investigations were undertaken on five radioactive minerals drawn from various parts of Peninsular India—namely, samarskite from Nellore (Andhra State), monazite from Mewar (Rajputana), and allanites from Madura

(Madras State), Purulia (Bihar), and Aanakapalle (Andhra State). Their physical and optical characters, autoradiographic pattern, and chemical composition were studied to determine their suitability for purposes of age determination. While samarskite has been found to be highly suitable (Aswathanarayana, 1953a), allanites from Purulia and Anakapalle are fairly so, but allanite from Madura (Aswathanarayana, 1953b), and monazite from Mewar are undependable as age indicators, as they have suffered leaching. The age data on the three suitable radioactive minerals together with some unpublished alpha-helium ages and published Rb-Sr and lead ages pertaining to the Precambrian rocks of India, are presented in the following tables.

The crude lead ages in the tables have been read from the family of curves of Wickman (1944).

The epithets "excellent," "good," "satisfactory," and "doubtful" have been used in the tables to connote specific degrees of dependability.

Excellent: Highly dependable, supported by isotopic analysis of lead.
Good: Dependable.
Satisfactory: Of the right order of magnitude, though not altogether dependable.
Doubtful: Too low, unlikely to be correct.

It is found that among the 36 ages listed, 16 are lead ages (5 excellent, 9 good, and 2 satisfactory), 18 are alpha-helium ages (9 satisfactory and 9 doubtful), and the other 2 are Rb-Sr ages (both satisfactory).

AGES OF THE ARCHAEAN OROGENIC CYCLES

In contradistinction to the approach of Fermor (1936), Holmes (1949, 1950) and Krishnan (1953) tried to arrive at the relative ages of the orogenies which produced the characteristic regional strikes of the Archaean structural provinces (N.E.-S.W. for Aravalli cycle, N.N.W.-S.S.E. for Dharwar cycle, N.E.-S.W. for Eastern Ghats cycle, and E.N.E.-W.S.W. for Satpura cycle). The age data are presented cycle-wise in tables 1 to 4, and all ages except those of doubtful nature are plotted on the structural map of India (fig. 1). Where alpha-helium age data are available from adjacent localities, the highest recorded age for the region has been plotted at a central location.

Aravalli and Delhi Cycles

Holmes (1949) delineated three orogenic cycles in Rajputana belonging to (1) the Gneissic Complex with N. or N.N.W. trend, believed to form a deeply denuded basement on which later formations were deposited, (2) the Aravalli orogenic belt whose N.E.-S.W. trend becomes N.-S. in the proximity of the Champner series and changes to N.N.W.-S.S.E. as the Deccan Traps are approached, and (3) the Delhi orogenic belt which is superimposed on the Aravalli belt and has the same regional trend. All the three orogenic cycles have produced pegmatites, and hence it is commonly difficult to fix up the geologic age of a pegmatite.

The pegmatites belonging to the Gneissic Complex and Aravalli orogenic belts are barren of radioactive minerals and hence cannot be dated by the lead method. But the trend lines of the Aravalli orogenic belt are helpful in

correlating it with the other Archaean belts. "In the Gujarat region, it (Aravalli strike) tends to splay out rather widely and a part of it, if continued, is directed towards Mysore in South India where the Dharwarian rocks have a dominant N.N.W.-S.S.E. strike. Though the area intervening between Gujarat and Mysore is covered by the Deccan Trap lavas, there appears to be little doubt about the direct connection between the Archaeans of the two areas" (Krishnan, 1953, p. 5). The breach in the trend of the Aravalli rocks in the Cambay-Gujarat region was surmised to be due to faulting of the Aravallis (Krishnan, 1953, p. 5).

The post-Delhi pegmatites are highly mineralized and have yielded radioactive minerals like uraninite and monazite. Attempts have been made by the author to date the monazite from the post-Delhi pegmatites of Ajmer-Merwara but they proved unsuccessful. The autoradiograph clearly indicates that the mineral had suffered leaching, presumably of lead and uranium, in unknown quantities and hence is undependable as an age indicator. As could be expected, the mineral has given a low age.

Holmes (1949) dated the uraninite from Bisundni, Ajmer-Merwara, which yielded an age of 735 ± 5 M.Y. for the Delhi pegmatitic cycle. The AcD/RaG, RaG/U, AcD/U, ThD/Th have given very closely agreeing ages and hence the above age can be regarded as of "first-class reliability."

Dharwar Cycle

The ages obtained by using the lead, alpha-helium and Rb-Sr ages are given in table 1.

Lead ages.—The monazite from the pegmatites of Yediyoor (Bangalore) gave a crude age of 1850 M.Y. (Holmes, 1951). The lead in the mineral was subsequently analyzed isotopically. From the 204, 206, 207, and 208 lead contents, Holmes (1955) deducted the "inherited lead," which he took from the isotopic analysis of lead from Chitaldrug galena, and calculated the percentage of radiogenic lead in the monazite. The 207/206 age was read from the nomographs of Wickman (1939). Other ages were calculated by the formulae given by Keevil (1939). The spread of the ages is as follows:

207/206	206/U	207/U	208/Th
2300 ± 100	1430	1810	1800 ± 40

It is seen that the four ages given above markedly deviate from the crude age, which is strongly indicative of the altered nature of the mineral. Such a spread of the ages could be brought about by (a) loss of lead, (b) loss of radon, and (c) any combination of (a) and (b). There is, however, direct evidence to show that loss of radon is negligible (Holmes, 1955).

When lead is lost, RaG/UI, AcD/AcU and ThD/Th give low values, RaG/UI giving a lower value than AcD/AcU. The above spread of the ages closely corresponds to this case, as 206/238, 207/235, and 208/232 ages are consistently lower than the crude age and 206/238 gives the lowest value of all. In such a case as this, the correct age is given by 207/206, which is 2300 ± 100 M.Y.

TABLE 1

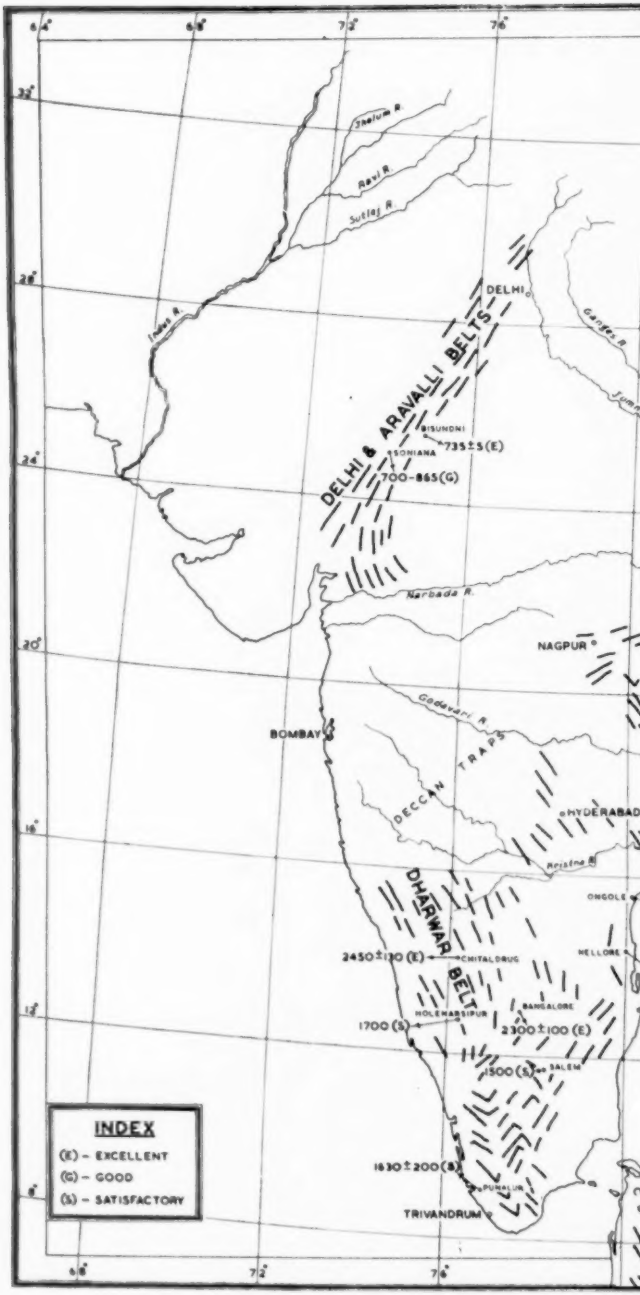
Dharwar Cycle

Serial no.	Name of the mineral or rock dated	Locality	Method of age determination	Age (in M.Y.)	Degree of dependability	Remarks
1	Monazite	Yediyoor, near Bangalore, Mysore	Pb-U-Th	2300 ± 100	Excellent	Based on the isotopic analysis of lead
2	Galena	Chitaldrug, Mysore	Lead isotopes	2450 ± 130	"	"
3	Magnetite crystals	Holenarsipur, Mysore	Alpha helium	1700	Satisfactory	Moderate helium loss
4	Magnetite-bearing chlorite schist	"	"	1600	Doubtful	Schist material must have lost an appreciable proportion of its helium content
5	Felspathized hornblende schist	"	"	1400	"	Extensive helium loss
6	Chlorite schist	"	"	1250	"	"
7	Hornblende schist	Kolar Gold Fields Mines, Mysore	"	1400	"	"
8	Quartz vein	"	"	600	"	"
9	Phlogopite	Punalur, Travancore	Rb-Sr	1630 ± 200	Satisfactory	"

1, 2—Holmes, Arthur (1955).

3-8—Unpublished ages (obtained by Prof. R. S. Krishnan and his associates on materials earlier studied by the author).

9 —Venkatasubramanian, V. S. (1953).


Jhelum R.
Ravi R.
Sutlej R.
Indus R.
DELHI
Ganges R.
DELHI & ARAVALLI BELTS
BISUNDNI
735±5 (E)
SONIANA
700-865 (G)
Narbada R.
NAGPUR
Godavari R.
BOMBAY
DECCAN TRAPS
HYDERABAD
Krishna R.
ONGOLE
DHARWAR BELT
2450±120 (E)
CHITALDRUG
NELLORE
HOLENARSIPUR
BANGALORE
1700 (S)
2300±100 (E)
1500 (S)
SALEM
INDEX
(E) – EXCELLENT
(G) – GOOD
(S) – SATISFACTORY
1630±200 (S)
PUNALUR
TRIVANDRUM

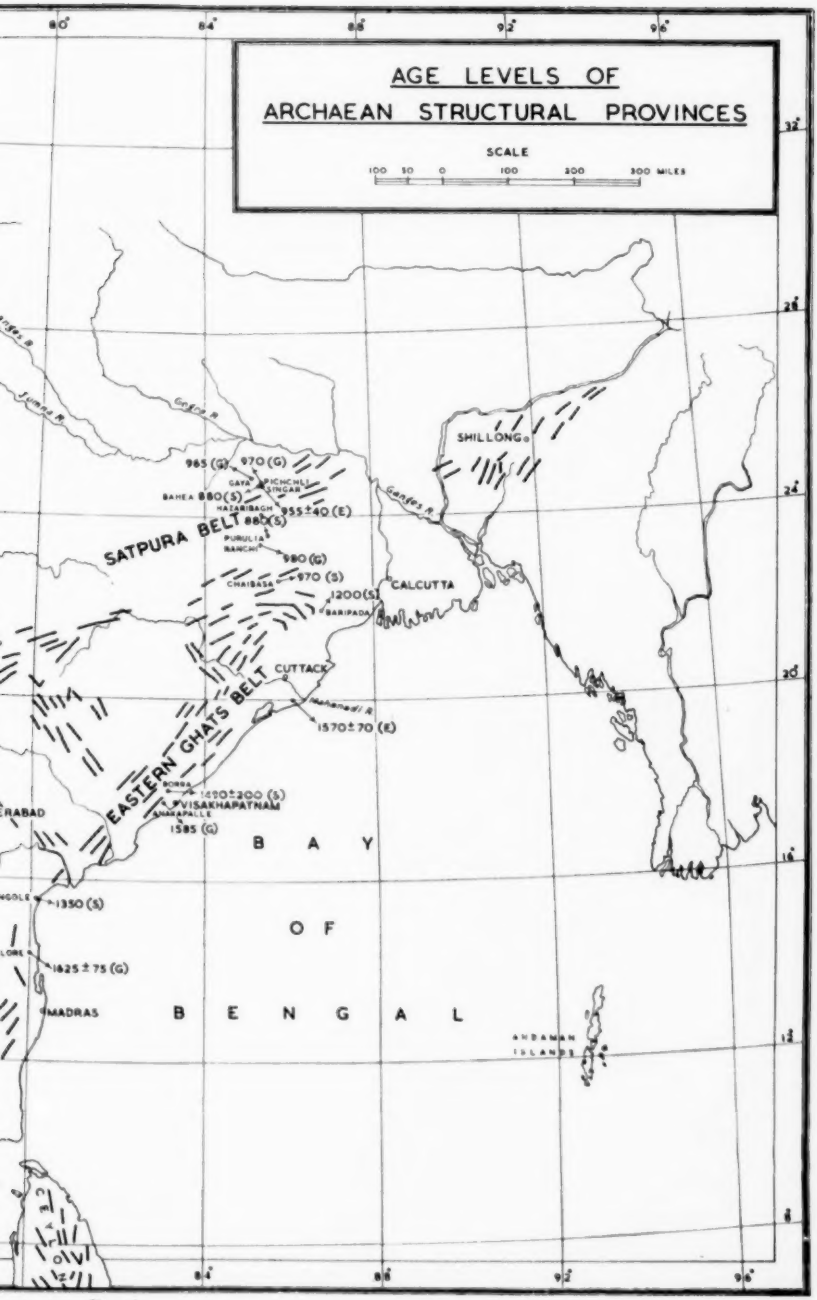

AGE LEVELS OF
ARCHAEAN STRUCTURAL PROVINCES
SCALE
100 50 0 100 200 300 MILES
SATPURA BELT
EASTERN GHATS BELT
SHILLONG
CALCUTTA
CUTTACK
VISAKHAPATNAM
MADRAS
B A Y
O F
B E N G A L
ANDAMAN ISLANDS
965 (G)
970 (G)
GAYA
PICHCHLI SINGAR
BAHEA 880 (S)
HAZARIBAGH
955±40 (E)
885 (S)
PURULIA
RANCHI
980 (G)
CHAIBASA
970 (S)
1200 (S)
BARIPADA
1570±70 (E)
1490±200 (S)
1585 (G)
1350 (S)
1825±75 (G)
Ganges R.
Jumna R.
Mahanadi R.
80°
84°
88°
92°
96°
32°
28°
24°
20°
16°
12°
8°

Fig. 1

The age of 2300 ± 100 M.Y. is an excellent agreement with the age of the Chitaldrug galena (2450 ± 130 M.Y.—as dated from the isotopic analysis of the lead), since the gold-galena veins are likely to be older than pegmatites.

The age of 492 M.Y. given by Bowie and Horne (1953) for cheralite (a mineral belonging to the monazite family, from Kattakuzhi, Travancore) was first considered anomalous by the author because of its low magnitude, but Professor Holmes, in a personal communication, pointed out that it is of the same order as that of thorianites from Ceylon with an age of 485 M.Y. The marked similarity in the ages of these minerals is strongly suggestive of the existence of a pegmatitic cycle common to both South India and Ceylon. Such a conclusion is in keeping with the geological history of the two regions.

Alpha-helium ages.—The age of the magnetite from Holenarsipur (1700 M.Y.) is the highest among the alpha-helium ages for Dharwar rocks and minerals. Hornblende schist and chlorite schist from Holenarsipur and hornblende schist from the Kolar Gold Fields Mines have given consistently low values, which is not surprising as the well-developed cleavages of the constituent minerals are highly conducive to helium leakage. As the stratigraphic age of the pegmatites and quartz veins examined is not clear, it is difficult to reach a conclusion on the degree of dependability of their alpha-helium ages but there is evidence to suggest that the ages are unlikely to be correct.

Rb-Sr age.—The age of the Travancore phlogopite (1630 ± 200 M.Y.), which occurs in the pyroxenite dikes at Punalur and Neyyoor, is interesting. The occurrence of the mineral where the Dharwar and Eastern Ghats strikes join and the general strike (N.N.W.-S.S.E.) of the associated charnockites and leptynites (Subramanyam, 1941) have rendered it difficult to place the mineral in either the Dharwarian or the Eastern Ghats structural province. As the phlogopite from Visakhapatnam belonging to the undoubted Eastern Ghats province has given an age of 1490 ± 200 M.Y., and as the strike of the formations associated with the Travancore phlogopite is closer to the Dharwarian than to the Eastern Ghats strike, it may be argued that the phlogopite belongs to the Dharwar cycle. Alternately, the phlogopite can be considered to belong to the Eastern Ghats cycle on the ground that phlogopite-pyroxenite is not a characteristic Dharwar rock whereas it is associated with Eastern Ghats, especially in Ceylon (personal communication from Prof. Holmes). The available evidence, however, does not warrant any specific conclusion on this subject.

Eastern Ghats Cycle

The lead, alpha-helium, and Rb-Sr ages are presented in table 2.

Lead ages.—The lead ages given by samarskite from Nellore, allanite from Anakapalle, and detrital monazite from Cuttack (207/206 age) do not differ much. An age of 1625 ± 75 M.Y. can therefore be given to the Eastern Ghats cycle, taking into consideration the range of variations in the age data available.

Alpha-helium ages.—As could be expected, the alpha-helium ages for rocks and minerals of Eastern Ghats cycle vary within wide limits, depending upon the degree of retention of helium in each sample. While magnetites, in

general, yield satisfactory ages, rocks like charnockites, biotite schists, amphibolites, and pegmatites and minerals like felspar are found to be undependable age indicators, as they invariably lose helium.

The alpha-helium ages of magnetites from the same locality, as for example Ongole and Kanjamalai, are significantly non-reproducible. This can be explained by bringing in the results of investigations of Professor C. Mahadevan in Professor P. M. Hurley's laboratory at Massachusetts Institute of Technology. He found that there is a change in the age ratio with depth in the magnetite grains because, while the helium content remains fairly constant, the superficial radioactivity of the magnetite grains decreases steadily as the acid dissolves the outer layers. This highly significant observation, besides explaining the absence of good reproducibility in the alpha-helium age data in the table 2, also suggests that the cores of magnetite can be expected to yield dependable ages.

The magnetite quartzites of Ongole and Salem belong respectively to the Madras-Ongole province (no. 12) and Salem-Arcot province (no. 11) of Fermor (1936, p. 42). Both of them belong to the iron ore province of the charnockitic region and both are characterized by the Eastern Ghats trend (Krishnan, 1953, p. 4). The similarity in the magnitude of their alpha-helium ages, though not dependable enough for dating the Eastern Ghats cycle because of the loss of helium which may occur in ancient minerals, suggests that the iron ores of Ongole and Salem were deposited contemporaneously.

The similarity in the ages of the Anakapalle (1585 M.Y.) and Nellore pegmatites (1625 $\pm$ 75 M.Y.), which are intrusive into khondalites and mica schists respectively, constitutes additional evidence in favor of the surmise of Mahadevan (1949, p. 78) that the Nellore mica belt is a continuation of the khondalitic zone. The allanite-bearing pegmatites of Aanakapalle and the monazite-bearing pegmatites of Cuttack (which yielded detrital monazite) are both intrusive into khondalites of the Eastern Ghats and, significantly enough, the apparent lead age of the former (1585 M.Y.) is of the same order as the 207/206 age (1570 $\pm$ 70 M.Y.) of the detrital monazite. Thus the radioactivity age data, besides indicating the continuation of the Eastern Ghats from parts of Orissa down to Nellore and beyond, also suggests that the pegmatitic display which marks the closing stages of the Eastern Ghats orogeny is contemporaneous in the various parts of the Eastern Ghats.

It is relevant to refer here to the controversy raised by Holmes (1949, p. 299) regarding the age of the Nellore samarskite. He calculated the apparent ages from the U, Th, and Pb contents given by Sarkar and Sen Sarma (1946) and Karunakaran and Neelakantam (1948), which he found were 830 and 1550 M.Y. respectively. He therefore pertinently questioned the accuracy of the chemical analytical data on the ground that the Nellore samarskite cannot give such highly discrepant ages. Krishnan (1953, p. 7) also came to the same conclusion on the strength of the available geological evidence. It was subsequently shown by the author (1953a) that the apparent discrepancy in the ages was due to an unfortunate mistake regarding the locality from which the mineral was collected. Sarkar's analysis of samarskite

TABLE 2

Eastern Ghats Cycle

Serial no.	Name of the mineral or rock dated	Locality	Method of age determination	Age (in M.Y.)	Degree of dependability	Remarks
1	Samarskite	Nellore, Andhra	Pb-U-Th	1550	Good	Crude age
2	"	"	"	1615	"	"
3	"	"	"	1765	"	"
4	Allanite	Anakapalle, Andhra	"	1585	"	"
5	Detrital monazite	Cuttack Dt., Orissa	"	1570 ± 70	Excellent	207/206 age
6	Vanadium-bearing magnetite	Baripada, Mayurbhanj, Orissa	Alpha-helium	1200	Satisfactory	Moderate helium loss
7	Magnetite quartzite	Ongole, Andhra	"	1350 (1160)*	"	The proportion of magnetite in the rock is highly variable and since the helium retentivity index of quartz is low, it can affect the over-all helium retentivity index to an extent depending upon its content.
8	"	Konizedu, near Ongole, Andhra	"	1290 (1050)*	"	
9	"	North Arcot Dt., Madras	"	1150	"	
10	"	Salem, Madras	"	1050	"	
11	"	Kanjamalai, near Salem, Madras	"	1500	"	
12	Charnockite	Ongole, Andhra	"	950	Doubtful	Highly active. Accessory radioactive minerals appear to have raised the specific activity of the rock, thereby lowering the helium age.
13	Pyroxenite	Kanjamalai, near Salem, Madras	"	1315 (1300)*	Satisfactory	The compact nature of the rock appears to be responsible for its moderate helium retentivity.
14	Pegmatite	Nallipalaiyam, Madras	"	880	Doubtful	Extensive helium loss
15	Pink felspar	Iddapadi, Madras	"	570 (500)*	"	"

16	Garnetiferous pegmatite	"	"	400	"	High specific activity coupled with extensive helium loss have lowered the age.
17	Phlogopite	Borra, near Visakhapatnam, Andhra	Rb-Sr	1490 ± 200	Satisfactory	—

* The ages in the brackets indicate the results of independent observations. The higher of the two ages is given first.

1. Aswathanarayana, U. (1953).
2. Karunakaran, C., and Neelakantam, K. (1948).
3. Nandi, S. K., and Sen, D. N. (1950a).
4. Unpublished age (calculated from the analytical data provided by Mr. Ch. Leelanandam).
5. Holmes, Arthur (1955).
6-16. Unpublished ages (obtained by Professor R. S. Krishnan and his associates on materials earlier studied by the author).
17. Venkatasubramanian, V. S. (1953).

TABLE 3

Delhi Cycle

Serial no.	Name of the mineral or rock dated	Locality	Method of age determination	Age (in M.Y.)	Degree of dependability	Remarks
1	Uraninite	Bisundni, Rajputana	Pb-U-Th	735 ± 5	Excellent	Based on isotopic analysis of lead
2	Monazite	Soniana, Rajputana	"	700-865	Good	"

1. Holmes, Arthur (1949, p. 292).
2. Holmes, Arthur (1949, p. 294).

TABLE 4

Satpura Cycle

Serial no.	Name of the mineral or rock dated	Locality	Method of age determination	Age (in M.Y.)	Degree of dependability	Remarks
1	Uraninite	Singar, Bihar	Pb-U-Th	955 ± 40	Excellent	Supported by isotopic analysis of lead
2	Monazite	Gaya, Bihar	"	965	Good	Crude age
3	Allanite	Ranchi, Bihar	"	980	"	"
4	"	"	"	980	"	"
5	"	Babea, near Singar, Bihar	"	880	Satisfactory	"
6	"	Purulia, Bihar	"	880	"	"
7	Monazite	Pichehli, Bihar	"	970	Good	"
8	Magnetite	Chaibasa, Singhbhum, Bihar	Alpha-helium	970	Satisfactory	Highly active. High alpha index might have lowered the helium age.

1. Holmes, Arthur (1950, p. 21).
2. Sarkar, T. C. (1941).
3, 4. Sarkar, P. B., and Sen Sarma, R. N. (1946).
5. Nandi, S. K., and Sen, D. N. (1950b).
6. Unpublished age (calculated from the data provided by Mr. Ch. Leelanandam).
7. Nandi, S. K., and Sen, D. N. (1950c).
8. Unpublished age (obtained by Professor R. S. Krishnan and his associates).

is now placed under the Satpura cycle as the mineral came from Gaya and not Nellore as was mistakenly thought.

Satpura Cycle

The lead and alpha-helium ages given by minerals belonging to the Satpura cycle are presented in table 4.

Lead ages.—The isotopic analysis of lead from the uraninite of Singar could not give a definite age to the Satpura cycle. It could only suggest the limits of the age (912-995 M.Y.) and, averaging them, the age was given by Holmes (1950, p. 24) as 955 ± 40 M.Y. Monazites from the Gaya district and allanite from the Ranchi district have given ages which fall within these limits. Allanites from Bahea and Purulia and samarskite from Gaya have yielded slightly lower ages than the rest.

Alpha-helium age.—The magnetite from Singhbhum has yielded an alpha-helium age of 970 M.Y. which is less than the alpha-helium age (1350 M.Y.) of the magnetite quartzites of Ongole belonging undoubtedly to the Eastern Ghats province. The age is termed satisfactory because, though it ought to be greater than that of Satpura pegmatites, which are later intrusives, it is only of the same order. The high specific activity of the mineral appears to have given it a low apparent age.

It is known that parts of the Shillong series show a Satpura strike and parts an Eastern Ghats strike; hence, it will not be surprising if further researches show that parts of the Shillong series belong to the Satpura cycle, and parts to the Eastern Ghats cycle.

CONCLUSIONS

A tentative succession of Precambrian diastrophic cycles for India, based on the available radioactive ages, is given below:

Vindhyan

735 ± 5 M.Y.

Delhi cycle (= ? Cuddapah)

955 ± 40 M.Y.

Satpura cycle

1625 ± 75 M.Y.

Eastern Ghats cycle

2300 ± 100 M.Y.

Dharwar cycle (= Aravalli cycle)

Older Gneissic Complex

These conclusions, based on the available radioactive age data for the Archaean orogenic cycles, are fully supported by the structural evidence. Krishnan (1953, p. 86) suggests that (1) the Dharwarian trend is a continuation of the Aravalli trend, (2) the Eastern Ghats trend is younger than the

Dharwarian as it is superposed on (and flows around) the latter, and (3) the Satpura trend is younger than that of the Eastern Ghats as is evident from their interrelation in Gangpur State.

The recent advances in the field of measurement of geologic time by radioactivity methods have greatly facilitated the bringing together of the two distinct, but nevertheless mutually related approaches—correlation of the rock formations and dating of the orogenic cycles. The K_{40}/A_{40} and K_{40}/Ca_{40} methods of dating potassium-bearing rocks, the lead method for determining the age of the accessory zircons in acid and intermediate rocks, and the Rb-Sr method for dating accessory biotite in rocks have now made possible the estimation of the ages of the rock formations directly, thus facilitating correlation in the sense of Fermor (1936). All these methods together with the classical lead methods, Pb-210 method, and the method of radiation damage in zircons can be used to date the pegmatitic minerals, and through them the ages of the orogenic cycles, in the sense of Krishnan (1953) and Holmes (1949, 1950). The two sets of data are directly comparable as they have been arrived at by the application of similar methods.

FURTHER WORK

The present investigations have served the useful purpose of dating the four major Archaean structural provinces of Peninsular India and have thereby laid the basis for detailed investigations on the correlation of the highly complex Archaean formations in the various parts of India. Kohman and Saito (1954) have recently given a succinct account of our present state of knowledge on the theory and techniques of measurement of geologic time, which shows that the Archaean rocks are capable of providing several age indicators.

Investigations are in progress on Archaean correlation problems, which, while making full use of correlation criteria like petrology, mineragraphy, grade of metamorphism, petrofabric pattern, etc., permit considerable scope for using the radioactive decay process as a yardstick of measurement of geologic time (by the application of the lead, potassium, and Rb-Sr methods). It is hoped to obtain thereby a correlation table, largely based on geologic criteria and suported in most cases by radioactive ages of absolute nature.

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A STUDY OF CHALCEDONY

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ABSTRACT. Recent experimental work has not tended to support the hypothesis that chalcedony contains interstitial opal. Instead, the results seem to show that chalcedony is essentially microcrystalline quartz with submicroscopic pores. The "quartz-with-holes" theory, however, does not explain the chemical reactivity of chalcedony, its biaxial character, or the suppression of heat effects near the high-low inversion point of quartz.

Chalcedony often appears brown under the microscope because light is scattered by submicroscopic pores. The occasional disintegration of chert in freezing is related to the fact that chert may contain interconnected pores of different sizes.

Chalcedony consists of quartz crystallites somewhat misoriented, more so from fiber to fiber than within fibers. Differences in orientation are normally adjusted by means of a transitional structure. The fiber interface is marked by a set of dislocations or islands of bad fit, and an elastically strained region extends to some distance away from the boundary. On the other hand, large angle misfit is common between bundles of fibers, and dislocations may be so closely spaced in the interface that it assumes the character of a thin vitreous layer. Water is probably associated with the regions of bad fit at the interface. Water also occurs in the relatively large pores visible under the electron microscope. This description of chalcedony is supported by optical evidence of strain, etching tests, infrared absorption spectra, and effects observed when chalcedony is raised to high temperatures.

A vapor pressure gradient exists in particles of chalcedony being heated at a finite rate. Water lost at high temperatures probably represents both water originally mechanically trapped and water originally chemically bonded to quartz. Water vapor persists in particles heated for prolonged periods at temperatures as high as 800 and 900 degrees C. Heat effects near the high-low inversion point of quartz are masked because of the strained condition of the material and because of the pressure gradient.

INTRODUCTION

In their contribution to the subject of chert, Folk and Weaver (1952) divide the microforms of quartz into microcrystalline quartz composed of interlocking grains in random orientation, and chalcedonic quartz consisting of radiating or sheaf-like bundles of fibers. According to Pettijohn (1949), the individual grains of chert, under highest magnification in the light microscope, show a fibrous, wavy extinction which is different from that of adjacent grains. Chalcedony appears to be quite generally characterized by either fibrous or undulose extinction. Practically all particles exhibiting one or both of these properties, however, have refractive indices less than those of quartz. Hence, when it is difficult to establish whether a very small grain of chert is fibrous or whether it is a single homogeneous quartz crystal, the refractive index may be used to discriminate between quartz and chalcedony. If any refractive index of the substance, as observed under the microscope, is less than n_ω of quartz, it may be termed *chalcedony* or *chalcedonic quartz*, provided it is not one of the other recognized forms of silica. Evidence given below, however, suggests that there is no sharp break between quartz and chalcedony. In principle at least, chalcedony may grade imperceptibly into quartz, and therefore the classification of the material may sometimes be a matter of personal preference.

Sosman (1927, p. 272) stated that chalcedony is a submicroscopic mixture of fibers of quartz and interstitial amorphous silica. A variable amount of water may be present but is not essential. Correns and Nagelschmidt (1933) and Donnay (1936) are in general agreement with this view. According to Donnay, the interstitial material is most likely opal. Correns and Nagelschmidt

consider that each quartz fiber is composed of a large number of quartz crystallites always arranged with c-axes perpendicular to the length of the fiber. The apparent birefringence varies along the length of the fiber because the c-axes may be at angles of zero to ninety degrees with reference to the microscope axis, although they are always essentially normal to fiber length.

That chalcedony contains interstitial amorphous silica or opal has been disputed by later workers. According to Folk and Weaver, as well as many other investigators, chalcedony gives a quartz X-ray diffraction pattern. From examination of chalcedony peels under the electron microscope, Folk and Weaver concluded that the characteristic lowered refractive index and density are fully explained by the presence of a large number of bubbles ranging in diameter from about 0.02 micron to about 0.30 micron. The bubbles are presumably filled with water. Midgley (1951), citing sensitive X-ray diffraction data that appear to exclude significant amounts of opal in chalcedony, and otherwise following a different line of investigation, reached substantially the same conclusions as Folk and Weaver. Thus, in the view of recent investigators, chalcedony would seem to be essentially microcrystalline quartz with submicroscopic pores.

Chalcedony, however, has a number of properties that appear anomalous in the light of this hypothesis. Most important among these is probably the chemical reactivity of the mineral with alkalies, as demonstrated in studies of the deterioration of concrete constructed with portland cement. For example, Mather (1951) made an exhaustive examination of cracked concrete in the Tuscaloosa Lock on the Warrior River in Alabama. He concluded that the cracking resulted from a chemical reaction between the alkalies of portland cement and chalcedonic chert. Other natural materials that react with portland cement in the same way as chalcedony are opal, glassy igneous rocks, and possibly tridymite and certain zeolites. Very little is known about the effects of tridymite and zeolites, and whether a reaction actually occurs is uncertain, but the evidence for opal and glassy rocks is abundant. Hanson (1944) and McConnell et al. (1950) have investigated the mechanism of cement-aggregate reaction. McConnell and colleagues state (p. 246):

"During the mixing of the aggregate, cement and water, and during the following several hours, the water acquires significant portions of the alkalies from the cement because of preferential solubility. As the hydration of the calcium silicates and aluminates progresses, the alkali concentration of this solution increases through the extraction of water. In this manner strongly caustic solutions form in the concrete during the period of set and the subsequent period of curing.

"Susceptible aggregate particles are attacked by the caustic liquid in the concrete, and alkalic silica gels begin to form. The reaction proceeds most rapidly for highly reactive materials, such as opal, and more slowly for less reactive ones, such as glassy volcanic rocks. During their early history, the gels are probably highly viscous, but their viscosity is decreased as water is imbibed from the paste.

"As a consequence of the formation of gels and their imbibition of water, osmotic pressures accumulate, producing stresses which distend and

may ultimately rupture the paste immediately surrounding the reactive particle."

Since pure, finely divided quartz does not react with alkalies to cause expansion and fracturing of concrete as opal and glass do, the observed reactivity of chalcedony tends to support the earlier hypothesis that interstitial opal is present.

Although the tendency of chert particles to disintegrate in freezing is probably not anomalous in view of the porous nature of chalcedony, a rather special combination of conditions must exist before significant disruption can occur. These conditions are discussed below.

Petrologically, perhaps the most puzzling feature of chalcedony is its behavior near the high-low inversion point of quartz. Sosman (1927) states that the absorption of heat due to high-low inversion of chalcedony begins at a lower temperature and extends over a wider range than in the case of quartz, although it ends at about the same upper temperature as in quartz. Tuttle (1949) found that two specimens of chert showed no break in the heating curve near 573°C., although X-ray analysis indicated that both samples were quartz. Keith and Tuttle (1952) believe that suppression of the heat effect associated with high-low inversion is caused by differential stresses set up in a mosaic of differently oriented grains. Such stresses have the effect of raising the inversion temperature of some crystal units and thereby spreading the heat effect over a considerable range of temperature. Keith and Tuttle pulverized novaculite specimens to the size of the individual crystals and obtained a measurable heat absorption where there had been none before. Midgley (1951) observed that although evidence of heat absorption in chalcedony is commonly present, it is not so pronounced as in quartz. He ascribes this difference to the small size of the crystals. In his view, small crystals require an induction period, varying with the size of crystal, before they can invert. Thus if the crystals are of variable size, absorption of heat will be spread over a temperature range.

In addition to refractive indices, other optical properties of chalcedony are abnormal relative to quartz. Jones (1952) found that iris agate composed of fibrous chalcedony is biaxial, positive, with $2E = 50 \pm 5°$. Winchell (1933) notes that the optic sign is uncertain and that the mineral may even be biaxial. The often-observed brownish color of chalcedony in transmitted light has not been adequately explained. Folk and Weaver (1952) ascribe it to an unspecified dispersion effect, caused by the difference in refractive index between bubble-filling material and quartz. The present writer has observed another anomalous optical phenomenon, not heretofore reported in the literature. Some cherts from the Tri-State lead and zinc district mounted in Lakeside no. 70 cement ($n_D = 1.5370$) appear to have a lower refractive index than when they are immersed in a standard index liquid ($n_D = 1.5400$). Fifty to sixty percent of the chert particles in Lakeside cement contained material with a refractive index less than the medium, whereas only twelve to twenty percent of the same particles in the index oil showed material with a refractive index less than the medium. This observation was confirmed by counts of several hundred particles in many different slides.

In summary, the present status of chalcedony appears to be as follows: recent work has brought to light considerable evidence against the interstitial opal hypothesis; but the alternative interpretation that chalcedony is an aggregate of quartz crystals with holes does not readily explain the reactivity of chalcedony with alkalies, the biaxial character of the material, and the suppression of heat effects near the high-low inversion point of quartz; in addition, the brown color in transmitted light, disintegration in freezing, and anomalous refractive index in certain media have not been explained. These properties of chalcedony are examined below. It will be found that the "quartz-with-holes" hypothesis accounts for the last three effects, but that a more general theory, incorporating this hypothesis, is required to explain all the properties of chalcedony.

CAUSE OF THE BROWN COLOR IN TRANSMITTED LIGHT

Some varieties of chalcedony appear brownish in transmitted light. Other varieties, particularly the long-fibered material found in agate, do not exhibit this property or do so only faintly and rarely. When the brown color is observed it can usually be demonstrated to follow from the Tyndall effect, i.e., scattering of light. Rayleigh's scattering formula (Valasek, 1949; Kraemer, 1930) is an approximate expression relating the intensity of the scattered light to that of the incident light:

$$I_s = \frac{I\,(n'-n)^2}{n^2}\,(1+\cos^2\Theta)\,\frac{\pi N V^2}{r^2\,\lambda^4} \quad . \qquad (1)$$

Here,

n' = refractive index of scattering particles (here the bubbles),
n = refractive index of embedding medium (here the quartz),
V = volume of scattering particles,
N = number of scattering particles,
λ = wave length of light,
r = distance from scattering region to observer,
I_s = intensity of scattered light,
I = intensity of incident light,
Θ = scattering angle.

Equation (1) shows that the intensity of scattered light varies directly as the square of the difference between the refractive indices of particles and medium and inversely as the fourth power of the wave length. Large particles scatter white light without altering its color but, as the size of the particles becomes smaller than the wave length of light, scattering increases as wave length diminishes, causing the scattered light to be blue in color. The transmitted light appears red or brown because of subtraction of the blue component.

To verify that the Tyndall effect is responsible for the brown color, the chert particles should be examined with an ordinary biological microscope under standard dark field illumination. In order to reduce or eliminate interference by an entirely different phenomenon described by Dodge (1948), the particles should be immersed in oil with a refractive index equal to or slightly less than the least index of the particles. An intense source of light such as a 100-watt projection lamp, without frosted glass diffusing disks,

should be used. Under dark field illumination only scattered, reflected, and highly refracted light will reach the eye. Light will be reflected or scattered without change of color by large pores. Smaller pores will scatter light of predominantly blue color. Occasionally, green or violet is observed, but the green appears to be limited to slightly iron-stained particles.

Although Dodge does not mention it, one of the photographs of his color plate seems to show chalcedony scattering light of substantially green hue. Dense light gray or tan chert from the Tri-State lead and zinc district and Meramec River chert also illustrate the phenomenon well.

FREEZING AND LOW-TEMPERATURE DEHYDRATION OF CHERT

In order to check the apparently anomalous refractive index of chert in Lakeside cement, mentioned above, the refractive indices of a number of samples of Lakeside cement scraped from slides in which the effect had been observed were measured by immersion in the liquids described in the appendix. All indices n_D were very close to but slightly less than 1.5373. Von Huene (1949), using a goniometer, found n_D to range from 1.5358 to 1.5371.

It was soon learned that the low refractive index of the chert particles, which was always associated with intensification of the brown color in transmitted light, was caused by dehydration. As shown by Folk and Weaver (1952, pl. 4, fig. 1), the light-colored chert from the lead-zinc deposits near Joplin, Missouri, is extremely porous, and the pores are interconnected. When the chert is heated, the pore water tends to be driven off, a process which is aided by the hygroscopic nature of the acid vapors formed when Lakeside cement is melted. Dehydration can best be demonstrated by heating the chert for a few minutes in concentrated sulfuric acid or by permitting it to stand for several days in cold concentrated sulfuric acid. When susceptible chert particles thus treated are examined in immersion oils, the brown color will appear greatly intensified and the mean refractive index will appear substantially lowered. Oil tends to seep into the evacuated pores, however, so that dehydration effects will usually be totally eliminated in a few days. Similarly, most of the water can be restored to the acid-treated chert by heating it in distilled water for two hours at 95°C.

Cherts that lose substantial quantities of water when raised to temperatures somewhat greater than 100°C. are also likely to disintegrate in freezing. The basic requirement is a system of relatively small, water-filled, interconnected pores of differing sizes. The theory of freezing in hardened portland cement paste, which is such a system, has been discussed by Powers and Helmuth (1953). At any given temperature below 0°C. only water in pores above a specified size can freeze. Water in smaller pores does not freeze because higher pressures are developed therein by surface tension, which becomes increasingly important as the size of the water-bearing cavity decreases. Water freezing in a large pore expands and exerts a pressure that is transmitted to the surrounding water. The hydraulic pressure thus developed may cause dilation. In addition, unfrozen water in the neighboring region creeps by surface diffusion into the large pore already containing ice, where it

freezes. The pressures evolved as a result of these two processes are often sufficient to cause failure of the chert, particularly if it is already somewhat weakened by weathering. The mechanism is similar to frost-heaving in shales and soils.

THE STRUCTURE OF CHALCEDONY

The earlier concept of chalcedony—quartz fibers with interstitial amorphous silica—falls in one of the two broad classes of grain boundary theory discussed by Aust and Chalmers (1952). They state (p. 155) that the hypothesis of a thin layer of vitreous material between grains of different orientation is based primarily on the fact that grain boundaries in a metal behave as regions of high strength at low temperatures and high rates of deformation, and as regions of weakness at high temperatures and low rates of deformation. Such behavior is characteristic of amorphous materials. The vitreous layer theory implies that the properties of a grain boundary are independent of the orientation of the grains on either side of the boundary. On this ground, Aust and Chalmers cite very strong evidence against the theory. Read and Shockley (1952), after noting that in a *large* angle grain boundary the relations between atoms are similar to those existing in a liquid, so that a large angle grain boundary is equivalent to a layer of liquid a few atomic spacings in thickness, state, "However, the older theory of an amorphous phase of substantial width is now regarded as physically unreasonable."

It appears, then, that in order to understand the properties of chalcedony that depend on the behavior of crystals near boundaries, it may be necessary to abandon the idea of interstitial opal in favor of the structural concepts associated with the transitional lattice class of theories, the second class discussed by Aust and Chalmers. According to these theories, the degree of disorder at a boundary increases with the difference in orientation between the crystals. In discussing the structure of internal boundaries, Brooks (1952) states:

"If the difference in orientation between the two grains is small, it is readily visualized that practically all the atoms on the boundary may be brought into registry by elastic distortion of their neighbors. Thus small angle boundaries are characterized by relatively minor misfit energy on the boundary itself but with elastic strain extending to considerable distances away from the boundary. On the other hand, if the difference in orientation is large, there are many misfitting atoms on the boundary and the registry cannot be much improved by elastic distortion of the atoms farther away. Thus a large angle boundary is characterized by a high atomic misfit energy and relatively little elastic misfit distortion away from the boundary. The transition, although much more severe, also takes place in a much shorter distance for large differences in orientation."

The dislocation model of grain boundaries has proved highly successful in predicting small angle boundary properties ($\Delta\Theta \leqslant 20°$). Read and Shockley (1952) show that, when two crystals differing only slightly in orientation are brought together, the method of joining that gives lower total energy is by an elastic distortion of the grains extending over relatively large regions,

the atomic disorder being confined to certain localized areas on the boundary. Thus a small angle grain boundary is viewed as an array of rather widely spaced dislocations in the surface of contact, set in a comparatively large three-dimensional elastically strained region. The concept is illustrated in figure 1 for the case of a simple cubic lattice.

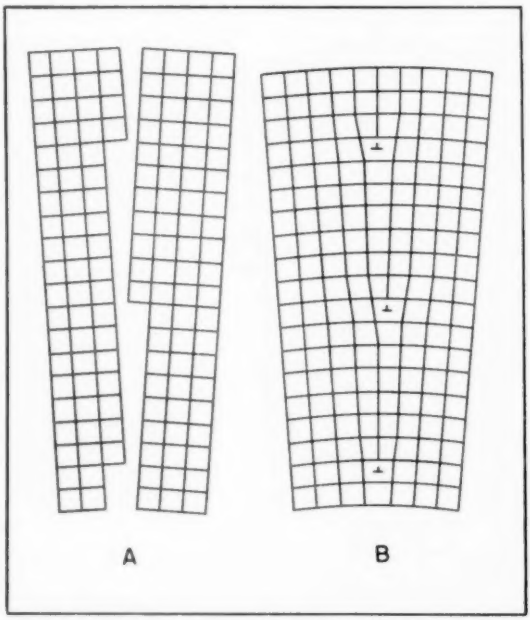

Fig. 1. Small-angle misfit of two cubic crystals. (A) Before joining. (B) After joining, showing strained lattice and arrangement of dislocations in interface (after Read and Shockley).

Although the foregoing theory has been applied mainly to metallic interfaces, there is no a priori reason to believe that the basic ideas are limited to this field. We may apply the model in a purely qualitative way to chalcedony and determine whether it accounts better for all the facts than either the interstitial opal or the porous quartz theories. As a starting point, we may assume the structure described by Correns and Nagelschmidt. They consider that a fiber of chalcedony consists of very small quartz crystals or crystallites lying with *c*-axes perpendicular to fiber length. The *c*-axes may tend to rotate along the fiber, so that when the fiber is parallel to the microscope stage, *c*-axes of some crystallites may coincide with the direction of the microscope axis, while others are at right angles to it. Moreover, because the fibers may not be perfectly straight, *c*-axes of the fiber may not all be parallel to the same vertical plane. Examination of well-developed fibrous chalcedony shows that change of orientation along the fiber due to this kind of rotation is very gradual.

Change of orientation from one fiber to the next may, however, be considerably sharper than intrafiber change. When chalcedony sectioned in the plane of the fibers is examined under crossed nicols, it is seen that two adjacent fibers, or two adjacent bundles of fibers in each of which the *c*-axes are nearly parallel, extinguish at different angles. Rarely the difference in extinction angle may be as high as 40°, but ordinarily it is considerably less than 20°. Thus at any point where two fibers are in contact, the *c*-axes of the respective fibers commonly fall in nearly the same vertical plane. Besides the horizontal change of *c*-axis direction from fiber to fiber, there exists a rotation of *c*-axes in the vertical plane. This is best revealed under inclined illumination. When the section is in a position such that the polarizer vibration direction is normal to fiber length, a relatively coarse relief pattern is visible. When the section is turned 90° on the stage, differences in relief disappear or become very faint. The relief pattern appears to correspond to bundles of fibers. Thus, within a comparatively short distance along a line normal to fiber extension, *c*-axes may change from a position nearly parallel to the stage to a position nearly perpendicular to it. The change of orientation along the line may be continuous. But if it is discontinuous, twinning may enter as an element in the transition. A possible twin plane is the $(11\bar{2}2)$ pyramid face. Although the adjustment is not necessarily made in this way, the possibility of twinning indicates that a high degree of disorder need not exist in the boundary between two bundles of fibers with sharply divergent *c*-axis orientation. If there is a tendency for adjacent bundles of fibers to adjust to radical orientation changes by twinning of individual fibers at the common boundary, it is not likely that perfect matching in the twin plane is often obtained.

In addition to the situations described above, misfit due to rotation of crystallites about their respective *c*-axes may occur both at fiber boundaries and within fibers. Misorientation of this kind can not be detected optically.

In the foregoing discussion we have assumed that *c*-axes are normal to fiber extension. Although this is a common structure in chalcedony, it is by no means universal. Actually, *c*-axes may be inclined at other angles to the fiber, and occasionally fiber and *c*-axis direction may coincide. These possibilities do not affect conclusions reached below concerning the nature of the interface between fibers.

It has also been tacitly assumed that the fibers are elongate prisms. Sometimes this is very nearly true (Jones, 1952, fig. 5). More often, however, the "fiber" of chalcedony is a thin spherical sector. Combinations of these give the fans and lenses seen in section. The spherical sector can be derived from small angle misfit of thin prisms, as illustrated in figure 1. If the orientation gradient is quite smooth, undulose rather than fibrous extinction is characteristic.

One other line of evidence remains to be considered. It is well known (Sosman, 1927) that quartz subjected to mechanical stress becomes biaxial. Strained quartz from metamorphic rocks also exhibits the property. Probably the simplest explanation of the optical anomalies of chalcedony, other than refractive index, is that they are strain-induced. Through the courtesy of

S. R. Austin the writer was able to examine the iris agate described by Jones (1952). This material, as Jones notes, is clearly biaxial, positive. The present writer found 2V to be somewhat variable, ranging from about 20° to 30°. Variability is to be expected if the biaxial property is caused by strain, the intensity of which may change from point to point.

The total evidence strongly suggests that crystallites in adjacent fibers commonly join by means of a transitional structure. The interfiber transition is marked by a set of dislocations or islands of bad fit in the surface of contact, and this surface is enclosed in an elastically strained matrix extending to some distance away from the boundary. The regions of bad fit probably accommodate impurities such as water, part of which may be chemically bonded to silica. Water may, of course, also occur in the relatively large pores seen under the electron microscope. On the other hand, the dislocations may be so closely spaced, particularly in the interface between bundles of fibers, that the interface assumes the character of a thin layer of liquid.

The general conclusion to be drawn from these considerations is that orientation differences are adjusted so as to minimize total energy. In some cases this leads to a strained lattice on both sides of the boundary; in other cases it leads to a thin vitreous layer between crystallites. If the foregoing analysis is correct, the principal zones of weakness in chalcedony must be parallel to fiber extension.

In banded and iris agate, however, some bands or parts of bands (these are always normal to fiber length) have noticeably lower refractive indices than other bands. It is clear from dark field examination that at least some of the low-index bands contain light-scattering pores. Low-index bands that do not exhibit scattering of light probably also contain pores, but of considerably smaller dimensions. The pores are not noticeably concentrated at fiber boundaries and do not appear to be associated on a microscopic scale either with increased strain or with greater atomic disorder in the surrounding region. Extinction patterns and certain etch patterns pass undeflected through these bands.

ETCHING TESTS

Chalcedony is somewhat soluble in pure water at 95°C. Analysis of distilled water in which chalcedony particles in the 45-76 micron range had been immersed for seventeen hours showed 5.1 milligrams of silica dissolved for each 100 milliliters of solution. Analysis was by the ammonium molybdate method. Transmission at 410 millimicrons relative to a similarly treated blank water sample was measured on a Beckman spectrophotometer.

Etching tests were made on polished specimens of this material, which was from sample C, in order to learn the source of the dissolved silica. Sample C is an agate nodule from an unknown locality in Montana. In hand specimen it appears translucent and of a faintly milky color. One or two thin, dark bands, transecting most of the nodule and parallel to its surface, are visible. Under the microscope it is seen to be of the long-fiber, iris type. However, the iris banding is poorly developed and often widely spaced. In dark field, the material appears faintly cloudy. The scattered light is very slightly, if at

all, reduced in wave length; and it appears essentially white. Some of the iris bands can be detected in dark field examination because they are cloudier than the average of the material. This condition may be due to greater concentration or greater size of pores, or both. The dark field appearance of this specimen is similar to that of samples A and B discussed below and contrasts strongly with that of many cherts, which commonly scatter light of pronounced blue color. Light transmitted through these agates is, of course, not noticeably changed in color.

The test specimens were ground flat on grooved cast iron laps by means of various abrasives, the last one used being American Optical Co. No. 305. They were then polished with Burrell "C-Ro" polishing compound on a soft cloth lap. Microscopic examination of the polished surfaces, the dimensions of which were about three-quarters inch by one inch, disclosed no structure. A few random scratches were visible, however.

One polished specimen was immersed in distilled water at 95°C. After six days only a slight intensification of the scratches could be detected. A small amount of dilute sodium hydroxide solution was then added to the distilled water. After fifteen hours the entire specimen had turned white and appeared deeply etched. Examination with a metalloscope revealed that alternate bands of chalcedony had been etched out. The banding developed by the sodium hydroxide treatment was parallel to the traces of banding originally visible in the material. Ordinarily but not everywhere, the etched bands were somewhat thinner than the bands on either side. The width of the relatively unetched bands ranged from about one millimeter to about one or two microns. Close examination of the material remaining in an etched zone showed it to be homogeneous, equigranular, and structureless. A few of the bands still retaining a polish displayed traces of fibrous structure normal to the banding.

Another polished specimen from the same nodule was steam-etched for one hour in a Cenco-Menzel autoclave, at a temperature of 417°F. and a pressure of 300 pounds per square inch. Examination of the treated specimen under a low-power stereoscopic microscope revealed a fibrous structure developed over several areas of random shape and size, none greater than fifteen millimeters in diameter. Examination in the metalloscope confirmed the fibrous pattern of the etch, which conformed in direction, magnitude, and general appearance with the underlying fibrous structure of the chalcedony. Prolonged examination failed to show any banding, except for a few uncertain traces practically at the limit of visibility. Because the fibrous pattern of this etch contrasted so strongly with the banding produced by sodium hydroxide treatment, the steam etch was repeated on another specimen from the same nodule. This time the sample was held for 2½ hours at the previous temperature and pressure. The results were the same. Small particles of chalcedony treated in the autoclave at the same time exhibited a small, but definite decrease in refractive index, indicating that water had been absorbed and that the material had expanded.

Clearly, one ionized water molecule can break the (Si-O-Si) bridge between two tetrahedra of the quartz structure to produce a weakly bonded or

essentially unbonded structure of the form (Si-OH OH-Si). One sodium ion with one hydroxyl ion can also break the bond between two tetrahedra. If the quartz is unstrained there should be little or no tendency for either event to occur. If the material possesses considerable strain energy the situation is otherwise. Many explanations, differing in details, can be advanced concerning the mechanism of solution in strained or disordered quartz. A possible, but perhaps considerably oversimplified picture is the following:

Assume a water molecule at the edge of a pore in a region under tension. When the temperature is raised the water molecule may approach an oxygen atom binding two silicon atoms. If the structure possesses sufficient strain energy the molecule will ionize; the hydrogen ion will be taken up by the oxygen atom; and the hydroxyl ion will become attached to one of the silicon atoms. Because the material is under tension, it will pull apart slightly when the bridge at this point and at others in the vicinity is broken. Thus other water molecules may filter through and repeat the process deeper in the structure. This reaction is the reverse of condensation polymerization of silicic acid. According to Carman (1940), there is a constant tendency for irreversible interaction of hydroxyl groups in solutions of silica, leading to formation of water and Si-O-Si linkages:

$$\text{-Si-OH} + \text{HO-Si-} \rightarrow \text{H}_2\text{O} + \text{-Si-O-Si-}.$$

If chalcedony has the structure proposed in the preceding section, the reverse reaction appears probable.

Whatever the details of the solution process may be, it is clear that the solvent action of NaOH is largely confined to the more porous bands of chalcedony. Under conditions prevailing in the steam etch, on the other hand, water is able to infiltrate the material and dissolve silica from the strained and disordered regions without regard to the presence or absence of relatively large pores. The different patterns produced by the two kinds of etching may be explained on the following basis. Water at room temperatures and below is characterized by considerable short range order (Gurney, 1953, p. 46-49). The degree of order falls off with rising temperature, and in the vapor phase water exists as single, unpolymerized molecules. These molecules are small enough to pass freely through most of the holes associated with dislocations. Accordingly, solution effects in the steam treatment are not limited to the vicinity of porous bands. On the other hand, both the Na^+ and the OH^- ions are order-producing ions (Gurney, 1953, p. 176, 250). They are able to set up and maintain an arrangement of local order in the surrounding water that is somewhat more stable than that of pure water. We may assume that the dimensions of the ordered envelope are roughly the same as those postulated by the older theory of "hydrated" ions (Dean, 1948). The radius of the sodium ion plus envelope would then be about 8 A.U. The envelope about an order-producing ion should be visualized from the statistical standpoint. That is, Na^+ and OH^- diffusing through water do not carry the same water molecules with them throughout their passage—the envelope tends to break up and reform continuously. Because of this tendency of sodium ions to develop a "co-sphere" of interlocking or polymerized water molecules, the probability that Na^+ enters channels much smaller than about 16 A.U. in

diameter is small. It is more likely that Na^+ ions will be captured by silica exposed at the surface of larger pores and capillaries. The solvent action of NaOH should thus be limited to a thin layer of material at the surface of relatively large cavities. After the first layer has been dissolved, the next can be attacked, and so on. Despite the lesser penetrative power of NaOH, its solvent and disruptive effects are more pronounced than those of water. Perhaps this is due largely to the greater ionization of the NaOH solution. But another factor may also play an important role. The sodium silicates formed by attack of the alkali probably do not diffuse outward as rapidly as they are formed. The concentration of sodium silicate in the pores may then attain values tending to promote polymerization and precipitation of colloidal matter. If reaction products can be immobilized by this mechanism, continued influx of NaOH under its potential gradient may develop pressures large enough to fracture the pore walls.

Frederickson and Cox (1954) and Frederickson (1955) have held quartz crystals in distilled water at elevated temperatures and pressures. They ascribe the observed solubility of quartz to its mosaic structure. Their conceptions of the quartz-quartz interface and of the mechanism of solution differ, however, from those suggested here. They consider that two adjacent, slightly misoriented blocks of the mosaic are held together by a continuous cement which exists in a strained or slightly disordered condition. The present writer is unable to follow their theory of solution; the reader is therefore referred to the Frederickson and Cox paper for details.

The results of the etching tests are incompatible with the unmodified interstitial opal hypothesis. According to this hypothesis, the low-index bands must contain more opal than the high-index bands; hence, they are etched out when treated with NaOH. But if the hypothesis is true, they should also be preferentially etched in the steam treatment.

BEHAVIOR OF CHALCEDONY AT ELEVATED TEMPERATURES

In studying the dehydration of cherts in hot concentrated sulfuric acid, the writer occasionally and not very consistently observed a colorless isotropic substance of variable, low refractive index ($n_D < 1.490$), which appeared to have been extruded from the chert. Solubility tests in sodium hydroxide solution and refractive index comparisons with silica precipitated by hot acid from aqueous sodium silicate indicated that the isotropic material was amorphous silica. Rapid heating in air of the 150-300 micron fraction of an agate also produced silica as well-developed microlapilli.

These observations can be explained in terms of the hypothesis advanced in this discussion. When the water present in chalcedony, either in pores of the magnitude seen under the electron microscope or in smaller holes, is heated and develops high pressures, part of the disordered and strained material is dissolved and carried to the exterior of the grain, where it is precipitated.

The experiments described below were performed on samples A, B, and C. These are all examples of fibrous chalcedony, of the type known as agate. The source and description of sample C are given in the preceding section. Sample A is from near Sanish, North Dakota. Sample B is the iris agate

described by Jones (1952), probably from California. These materials are all similar, but they differ in details such as refractive index, development of banding, parallelism and length of fibers, etc. In hand specimen all appear somewhat translucent and of a faintly milky color.

Heating samples A, B, and C for two hours at 300°C. caused no measurable reduction of refractive index. Heating at 500°C. resulted in marked reduction of refractive index in all cases. For example, ω of sample B dropped from 1.535 to slightly greater than 1.528. The same material heated for two hours at 650°-675°C. showed further reduction of ω to somewhat less than 1.528.

Water lost from sample A by heating for 1½ hours at 500°C. was equal to 0.78 percent by weight. The water lost from sample C by heating for one-hour periods at various temperatures is given below:

Temperature, degrees C.	Cumulated water loss, percent by weight
300	0.06
500	0.84
700	1.10

Untreated material from sample C heated for seven minutes over a laboratory burner at about 900°C. lost 1.16 percent by weight of water. All the foregoing tests were made on the 45-150 micron fractions of the respective samples. Rate of temperature rise, except in the last experiment, was about 10°C./min.

Relatively coarse particles of sample C (about ¼-inch size) held for one hour at 500°C. lost only 0.36 percent of water. Length measurements on representative particles before and after heating showed no change of particle size. This result is in accordance with the principle that water releasable at a given temperature is not lost instantaneously when that temperature is reached. Hence, a water concentration gradient must exist in any particle being heated at a finite rate. The concentration of water is greatest near the center of the particle and least near the surface. Consequently, a pressure gradient also exists in the particle, the pressure due to water vapor being greatest at the center and least at the surface. The observed deviation in water loss may also indicate that a large grain can not lose as much water as a small one when both are heated indefinitely at the same temperature. But this possibility does not affect the conclusion that particles being heated develop pressure gradients.

If the rate of heating is rapid, or if the particle is large and the rate is slow, water present in small pores or "bound" water released from close association with the structure will cause a permanent expansion of the particle. Length change of two-millimeter particles of sample A heated rapidly to 900°C. was found to be about plus two percent. Similarly, when the large particles of sample C, which had been heated at a rate of about 10°C./min. to 500°C. and held at this temperature for one hour without incurring length change and without developing internal bubbles, were heated at the same rate to 700°C., considerable enlargement took place. The length change was not

measured, however, because the particles had many radial, pie-shaped cracks. The cracks indicate that expansion near the center of the particle was greater than near the surface, in accordance with the pressure gradient deduced above. On the other hand, if the rate of heating is so rapid that practically no water escapes during the expansion, the concentration of water remains nearly uniform throughout the grain, and no radial cracks develop. Examination of particles expanded under various conditions shows that the interior of the particle is brown in transmitted light and that the mean refractive index is variable, ranging from as low as 1.470 to as high as 1.528. Thus the refractive index of heat-treated chalcedony is a function, among other factors, of size of particle, rate of heating, temperature attained, and original water content.

Not all the water released and converted to vapor at a given temperature can be driven from the particle, even if it is held at that temperature for as long as two hours. Examination in transmitted light of the 45-150 micron fractions of all three samples heated for at least one hour at 700°C. shows that a variable proportion of the grains have brownish interiors that are enclosed by clear, colorless rims. The percentage of such particles increases with increasing size until it reaches 100 percent. Dark field examination discloses the following sequence from surface to core: a clear, non-scattering outer shell; a pale white, cloudy shell, similar in appearance to the untreated material; a relatively bright, blue shell; and sometimes a brilliant white center. The sequence is of course gradational. Obviously the pore diameter ranges from zero near the surface to about microscopic dimensions near the center. The 45-75 micron fraction of sample B, previously heated to 650°C. and displaying the foregoing characteristics, was held for two hours at 800°C. The particles formerly characterized by gradational porosity then exhibited only a clear outer shell, which accounted for one-tenth to one-half of the radius, and a central region packed with bubbles of uniform size, about one to two microns in diameter.

Thus the particle appears to act as a closed system with respect to transfer of matter. The explanation of this phenomenon is believed to be approximately as follows: As the particle is heated and water is released, a pressure gradient develops. The released water is thought to represent water chemically bonded to silica, as in the (Si-OH OH-Si) break between tetrahedra, or water otherwise disseminated through strained and disordered regions, perhaps less directly tied to the silica framework, but at any rate not having the properties of the bulk liquid. If, after the pressure gradient is formed, the temperature ceases to rise and remains constant, the water vapor everywhere in the particle rapidly becomes saturated with silica. As the vapor moves from a high pressure zone to a low pressure zone, silica must continuously precipitate from it. In this way material is lost from near the center and is gained near the surface, so that the size of pores and capillaries through which the silica-laden vapor passes decreases monotonically outward. The greatest amount of material is deposited at the surface of the particle, where the flow of vapor is soon choked off. As soon as the thin, essentially impermeable outer shell is complete, the pressure in nearby regions behind it begins to rise because of

continued flow from the central region. But the vapor can not dissolve the seal because it is saturated with silica on arrival and because the system tends to assume a configuration such that its surface energy is minimum. Hence, the very smallest pores and capillaries—those on the inner side of the seal—close up, and the clear outer shell grows rapidly inward. Finally a "stable" state in which all the pores are equal in size is attained.

The outer shell is well developed on large particles of chalcedony heated at a rate of about 10°C./min. from 500°C. to 700°C. and held at the latter temperature for an hour. The clear material looks glassy in hand specimen. It represents silica with a greater atomic disorder content than normal chalcedony. Its mean refractive index is less than that of unheated chalcedony but greater than that of small heat-treated particles that do not develop the zoned structure.

The fact that water existing as vapor is held within the particle for indefinite periods at elevated temperatures makes it difficult to draw any conclusions concerning the nature of the water in chalcedony from measured water losses alone. That is, water lost at high temperatures is not necessarily water originally chemically bonded to silica. Other evidence, however, strongly suggests some kind of chemical bonding. Even small particles, in the 45-75 micron range, do not lose substantial quantities of water until temperatures greater than about 350°C. are reached. The sudden appearance of vapor bubbles between 500°C. and 700°C. may indicate a fairly rapid evolution of water vapor at some point in this temperature range. Probably monomeric and hydrogen-bonded OH occurring at a broken bridge between two tetrahedra would not be released until a temperature permitting some reorientation and recrystallization were attained.

Through the courtesy of Prof. W. D. Keller and Dr. E. E. Pickett, of the University of Missouri, additional information on the condition of the water in chalcedony was secured from infrared absorption data. Dr. Pickett obtained the spectrograms of samples A and C shown in figure 2. (Only the portions of the spectrograms between 2.0 and 6.5 microns are reproduced.) The samples were crushed in a mullite mortar, and the fractions less than two microns were extracted by pipette from distilled water suspension. The extracted fractions were dried for eight hours at 110°C. before being placed in the shipping containers. The infrared measurements were made in a Nujol mull, and the absorption peak at 3.4 microns is due to the Nujol. Professor Keller states that the absorptions between 2.7 and 3.2 microns indicate hydroxyl in monomeric and polymeric bonding. Water in the H_2O form is indicated by the absorption peak at 6.2 microns.

Interpretation of the spectrograms is complicated somewhat by the probability that water was absorbed during fractionation of the material. ("Absorption" rather than "adsorption" is used here to refer to the acquisition of water by chalcedony. Adsorption implies that a substance is taken up on pre-existing internal or external surfaces. As discussed above, however, new openings and new surfaces of discontinuity probably result from the solvent action of water.) It cannot be assumed that all absorbed water was eliminated by drying at 110°C. Hence, the infrared spectrograms not only

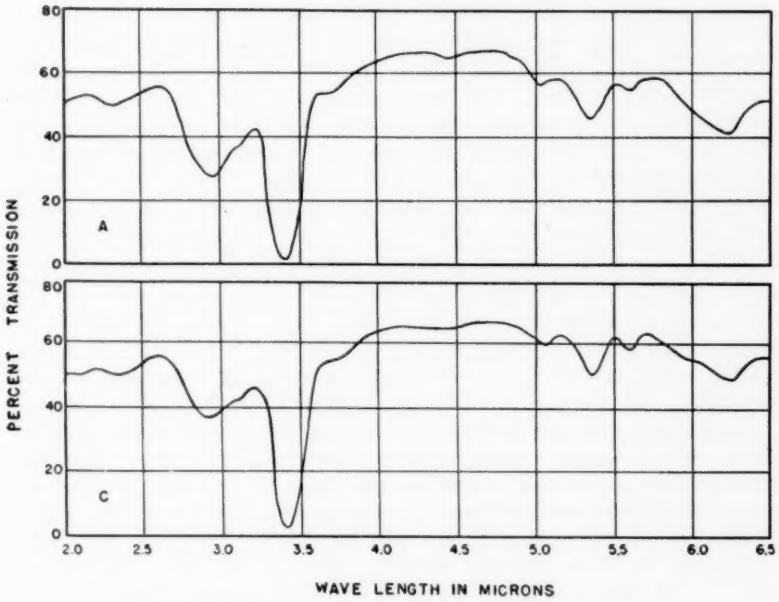

Fig. 2. Infrared absorption spectrograms of samples A and C.

indicate the condition of the water originally present in chalcedony but also probably furnish a clue to the mechanism of solution.

According to Keller and Pickett (1954), absorption of infrared radiation by monomeric OH reaches a maximum at 2.75 microns but diminishes almost to nothing at 2.8 microns. This absorption is prominent in kaolinite, for example. In chalcedony, monomeric OH should occur at the (Si-OH OH-Si) break between tetrahedra where, for one reason or another, no bond between the two hydroxyls exists. Polymeric OH, which characteristically absorbs at somewhat longer wave lengths in the 2.7-3.2 micron band, may occur in the same position. In this case the hydroxyls are connected by a hydrogen bond. Although mechanically trapped water may also be indicated by the absorption at longer wave lengths in the 2.7-3.2 micron band, the infrared data are consistent with the hypothesis that water bonded to silica is associated with dislocations at fiber interfaces. The data are also generally consistent with the theory of solution discussed earlier.

More detailed information on infrared spectra is contained in the 1949 and 1954 papers by Keller and Pickett, as well as in papers by Miller and Wilkins (1952) and Adler, et al. (1950).

The low-temperature dehydration experiments mentioned earlier show that ordinary liquid water is found in the light-scattering pores. If the pores are interconnected most of this water can be expelled by heating at temperatures not much greater than 100°C. If the pores are not connected, one of

two things may happen: the particles will explode when heated above 100°C., or the particles will not explode because water expelled from the pores will penetrate the silica framework, lodging at sites characterized by high atomic disorder or elastic strain. The steam-etching experiment tends to confirm the latter possibility. The refractive index of chalcedony particles in the 45-150 micron range decreased in this experiment, indicating that water had been absorbed and that the material had expanded.

Accordingly, some of the water lost at high temperatures may represent not only original chemically bonded water but also water expelled from relatively large pores at lower temperatures and immediately absorbed in disordered and strained regions. The pressures prevailing in the interior of the particle, along with the increased ionization of water at elevated temperatures, would tend to establish some type of chemical bonding between part of the expelled water and silica. Of course, some of the water discharged at high temperatures may have been essentially mechanically trapped at all times.

Two factors are probably responsible for the partial or complete masking of heat effects associated with high-low inversion in chalcedony. The first of these is the strained state of the material itself. Parts of the structure are under tension, and parts are under compression; hence, the inversion temperature should be spread over a range. The pressure gradient, for which considerable evidence has been adduced, enhances this effect. In heating, quartz in the outer portions of the particle is under tension, whereas quartz in the central region is under compression. Moreover, high vapor pressures in the interior of a particle imply that part of the water remains intimately intermingled with or bonded to quartz. Such water may interfere in some degree with inversion. Pulverizing of chalcedony would normally tend to increase strain and disorder, but if the final particles are very small, the strain may be reduced. Clearly, if grinding is carried far enough most of the effects arising from the pressure gradient will be eliminated. This explains the measurable heat effects obtained by Keith and Tuttle when they ground chalcedony to a fine powder.

CONCLUSIONS

(1) In view of recent advances in the theory of crystal interfaces, which have tended to discredit the concept of an interstitial amorphous layer between crystals of different orientation, the description of chalcedony as quartz fibers with interstitial opal may not be appropriate. Folk and Weaver (1952), in this country, and Midgley (1951), in England, have advanced experimental evidence that in some respects is inconsistent with the opal hypothesis. In the present investigation, optical anomalies attributable to strain and other evidence have demonstrated the need for a more precise theory of chalcedony.

(2) Although the "quartz-with-holes" theory adequately explains refractive index anomalies due to dehydration, the disintegration of chert in freezing, and the brownish color of chalcedony in transmitted light, the theory does not explain the weakening or absence of heat effects near the high-low inversion point of quartz, the etch patterns obtained in this investigation, the biaxial character of chalcedony, or its solubility and chemical reactivity.

(3) In so far as known, all the properties of chalcedony are consistent with the hypothesis that chalcedony is composed of quartz crystallites somewhat misoriented, more so from fiber to fiber than within fibers. Orientation differences are normally adjusted by means of a transitional structure. The result is a set of dislocations or islands of bad fit in the fiber interface, which in turn is enclosed in an elastically strained matrix extending to some distance away from the boundary. On the other hand, large angle misfit is common between bundles of fibers, and dislocations may be so closely spaced that the interface assumes the character of a thin layer of liquid. Water is probably closely associated with the regions of bad fit at the interface. Water also occurs in relatively large light-scattering pores.

(4) A vapor pressure gradient exists in particles of chalcedony being heated at a finite rate. Water lost at high temperatures probably represents both water originally mechanically trapped and water originally chemically bonded to silica. Gaseous water persists in particles heated for prolonged periods at temperatures as high as 800 and 900 degrees C.

(5) Heat effects are masked near the high-low inversion point of quartz because of the strained state of the material and because of the pressure gradient. In chalcedony crushed to very fine size most of the effects of the pressure gradient are eliminated; hence, small particles will exhibit heat absorption in a more limited temperature range than large particles.

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APPENDIX: IMMERSION LIQUIDS FOR DETERMINING REFRACTIVE INDICES OF LAKESIDE CEMENT AND HARDENED CANADA BALSAM

Because a goniometer was not available, it was necessary to use the immersion method in order to measure the refractive index of Lakeside no. 70 cement. This material is rather soluble in ordinary index media so that no reliable results could be obtained until, after some experimentation, a liquid consisting of the end-members castor oil and tricresyl phosphate was used. The latter is a plasticizer used in manufacture of vinyl paints and also as an additive in some brands of gasoline. Both Canada balsam and Lakeside cement are probably dissolved very slightly in mixtures of these liquids; however, the reaction is not fast enough to interfere with accurate refractive index determinations.

Mixtures prepared from these end-members are relatively stable after the first twenty-four hours. A slight shift from the originally observed index, of the order of 0.0005, usually occurs during the first day, but the value obtained at the end of this period appears to persist indefinitely. The vapor pressures of the end-members are low and approximately equal. A small quantity of one mixture kept for twenty-four hours in an open beaker showed no index change whatever. On the other hand, mixtures of alpha-chloronaphthalene and diethylene glycol mono-n-butyl ether exhibited marked changes after ten minutes exposure to air.

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CORRELATION OF CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF DOLOMITE*

E-AN ZEN

ABSTRACT. Regression equations relating the chemical composition of a nearly-pure dolomite with its ordinary index of refraction and its cleavage-rhomb spacing have been derived by the method of least squares. Predictions based on the equations are in accord with observations. On the basis of these equations the partial molar volumes of the several components in dolomite have been derived and these are shown to differ from the molar volumes of the corresponding pure carbonates. The volume data suggest strong pressure dependence of the compositions of coexistent calcite-dolomite pairs. Theoretical considerations show that studies on the compositions of phase-pairs possessing such properties are capable of yielding unique information on the temperature and pressure of their crystallization. Such phase pairs, therefore, are useful in the study of rock metamorphism.

INTRODUCTION

The mineralogy of rock-forming carbonates has been studied by various authors. In order to render such studies useful to the geologist, however, means must be devised whereby the composition of a carbonate can be predicted from its physical properties. An early attempt in this direction was made by Ford (1917). Ford, however, presented the data available to him without critical examination of the samples. Moreover, the X-ray technique of measurement of cell dimensions was not generally available at that time. It is desirable, therefore, that a new correlation of data be attempted.

In this paper we first develop a general method of treatment of the data, and then apply it in simplified form to a few selected, analyzed dolomites to obtain regression equations. From these relations properties of the volume-behavior of the components in dolomite are deduced, and application of the results to petrology discussed.

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METHOD OF TREATMENT

The important rock-forming carbonates are phases in the four-component system: $CaCO_3$—$MgCO_3$—$FeCO_3$—$MnCO_3$. Since only three of these mole fractions are independent variables, three independent physical properties

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are needed to ascertain the chemical composition of a given carbonate. For calcite and dolomite low in iron and manganese, we can group these two components together to a very good approximation. Only two physical properties are now required. We shall use the following, chosen because they are easy to measure accurately.

$$\begin{aligned} d_{(10\cdot4)} &= f_1(N_{CaCO_3}, N_{MgCO_3}, N_{FeCO_3}) \\ n(O) &= f_2(N_{CaCO_3}, N_{MgCO_3}, N_{FeCO_3}) \end{aligned} \tag{1}$$

where $d_{(10\cdot4)}$ is the interplanar spacing of the cleavage rhombs of calcite and dolomite;[1] n (O) the ordinary index of refraction (to be abbreviated *n* hereafter), and N the mole fraction.

We expand these functions in Taylor's series in terms of two of the mole fractions given in (1). The reference states of the expansions are taken to be pure calcite and stoichiometric magnesium dolomite. The expansion yields:

$$d_{(10\cdot4)}(N_i) = d^\circ(N_i^\circ) + \Sigma_i \left(\frac{\delta d}{\delta N_i}\right)_{N_i = N_i^\circ} \Delta N_i + \tfrac{1}{2}\Sigma_{i,j}\left(\frac{\delta^2 d}{\delta N_i \delta N_j}\right)_{N_i = N_i^\circ, N_j = N_j^\circ} \Delta N_i \Delta N_j + \ldots . \tag{2a}$$

$$n(N_i) = n^\circ(N_i^\circ) + \Sigma_i \left(\frac{\delta n}{\delta N_i}\right)_{N_i = N_i^\circ} \Delta N_i + \tfrac{1}{2}\Sigma_{i,j}\left(\frac{\delta^2 n}{\delta N_i \delta N_j}\right)_{N_i = N_i^\circ, N_j = N_j^\circ} \Delta N_i \Delta N_j + \ldots . \tag{2b}$$

where N_i refers to either of the independent mole fractions, the superscript zero refers to the reference state, and $\Delta N_i = N_i - N_i^\circ$. For later use, we also give the analogous expansion for the mean molar volume, V_M:

$$V_M(N_i) = V_M^\circ(N_i^\circ) + \Sigma_i \left(\frac{\delta V_M}{\delta N_i}\right)_{N_i = N_i^\circ} \Delta N_i + \tfrac{1}{2}\Sigma_{i,j}\left(\frac{\delta^2 V_M}{\delta N_i \delta N_j}\right)_{N_i = N_i^\circ, N_j = N_j^\circ} \Delta N_i \Delta N_j + \ldots . \tag{2c}$$

The molar volumes can be obtained from the (10*4) and the (0006) spacings (for dolomite) by means of the relation

$$V_M = \frac{12\sqrt{3}\, d_{(0006)} \times N_A \times 10^{-24}}{\left[\dfrac{9}{d^2_{(10\cdot4)}} - \dfrac{4}{d^2_{(0006)}}\right]} \tag{3}$$

where the volumes are in cubic centimeters, and N_A is Avogadro's number ($N_A = 6.0247 \times 10^{23}$; DuMond and Cohen, 1953, p. 706).

PRESENTATION OF DATA

In this paper, we shall deal only with dolomite. The data available to the writer justify only a first order (linear) approximation, namely,

[1] In this paper, the X-ray Miller indices are used in favor of the morphological indices. See Bragg, 1937, p. 115.

$$d_{(10\bar{1}4)}(N_i) = d^\circ(N_i^\circ) + \Sigma_i \left(\frac{\delta d}{\delta N_i}\right)_{N_i = N_i^\circ} \Delta N_i \qquad (4a)$$

$$n(N_i) = n^\circ(N_i^\circ) + \Sigma_i \left(\frac{\delta n}{\delta N_i}\right)_{N_i = N_i^\circ} \Delta N_i \qquad (4b)$$

and

$$V_M(N_i) = V_M^\circ(N_i^\circ) + \Sigma_i \left(\frac{\delta V_M}{\delta N_i}\right)_{N_i = N_i^\circ} \Delta N_i \qquad (4c)$$

We need hardly point out that the approximation of linearity between $d_{(10\bar{1}4)}$ and composition, even in the neighborhood of pure phases, is crude at best and is not even strictly consistent with the assumption of linearity of volume. It is further not to be confused with the assumption of ideal solution. "Vegard's Law" is intended for cubic crystals only (Vegard and Dale, 1928), and even there it does not express the condition of volume ideality (Zen, 1955).

Five dolomites, analyzed by standard "wet" procedures, were available for the present study. The chemical data are presented in table 1.[2] The measured properties, together with the computed mole fractions of the various components of these five dolomites, are presented in table 2.

The *d*-spacing data were obtained with the North American Philips High-angle Diffractometer, using a rotation speed of 0.25° 2θ per minute and chart speed of 0.5 inch per minute. The 2θ values can be read to $\pm$ 0.01°. The position of a diffraction line was measured in the following manner. The midpoints along the θ-coordinate for a given line were measured at a number of intensity levels, all above the noise level. The points were connected, the line was extrapolated to the noise level, and then drawn vertically down to the degree-marking line, where its 2θ value was measured. These line-positions were then compared with the line-positions of an internal standard quartz. Since the *d*-spacings of quartz are known with high precision (Parrish, 1948), the positions of the dolomite lines can be corrected for instrumental errors. The quartz lines used ($(2\bar{1}*1)$ and $(10*0)$) were chosen so as to bracket the dolomite lines of interest. The corrections were plotted against 2θ values, and finally the linearly interpolated corrections applied to the dolomite lines. Linear-interpolation was satisfactory since the corrections are usually no more than $\pm$ 0.01° 2θ. The *d*-spacings were determined from graphs based on the data of Switzer et al. (1948). Several independent measurements of the spacings were made on every dolomite and the results were found to be reproducible to the nearest 0.01° 2θ.

The index of refraction was measured using oil immersion mounts, and was checked several times over a period of days. The index of the matching oil was simultaneously measured on a calibrated Abbe refractometer. Sodium light was used in all determinations.

[2] The writer is indebted to Mr. A. H. Chidester for samples and analyses 1, 2, and 3; to Dr. R. I. Harker for sample 4; and to Professor H. Winchell for sample 5.

TABLE 1

Chemical Analyses of Selected Dolomites

	1	2	3	4	5
CaO	29.98	30.10	27.32	31.27	Ford (1917, p. 243) gave only proportions of the components; no chemical analysis available.
MgO	19.10	19.76	22.34	21.12	
FeO	2.65	2.09	1.16	0.22	
MnO	0.81	0.69	0.20	nil	
Fe_2O_3	0.64	0.58	0.35	tr.	
SiO_2	—	—	3.92	—	
CO_2	46.73	47.10	44.41	47.22	
H_2O	—	—	0.29	0.02	
Insoluble residue	—	—	—	0.12	
Total	99.91	100.32	99.99	99.97	

No. 1 from talc-carbonate vein, Waterbury Mine, Moretown, Vermont. U. S. G. S. sample #ID-50-1997-CDSW.

No. 2 from talc-carbonate vein, Johnson Mine, Johnson, Vermont. U. S. G. S. sample #ID-50-1998-CDSW.

No. 3 from serpentine grit, Barnes Hill Prospect, Waterbury, Vermont. U. S. G. S. sample #ID-50-1991-CDMSW.

No. 4 from Haley, Ontario. R. A. Howie, Manchester University, England, analyst. Harker and Tuttle, 1955, p. 216.

No. 5 from Vorderrheintal. Ford, 1917, p. 243.

No. 1 corrected for 0.57 formula % of magnetite of analyzed composition.

No. 2 corrected for 0.51 formula % of magnetite of analyzed composition.

No. 3 corrected for 5.34 formula % of talc and 0.31 formula % of magnetite of analyzed compositions.

TABLE 2

Data on Analyzed Dolomites*

Specimen no.	1	2	3	4	5
Mole fraction					
$CaCO_3$	0.5078	0.5053	0.4828	0.5142	0.5006
$MgCO_3$	0.4500	0.4616	0.5050	0.4830	0.4705
$FeCO_3$	0.0313	0.0240	0.0094	0.0028	0.0208
$MnCO_3$	0.0108	0.0091	0.0028	nil	0.0081
n(O) (Na light), ± 0.0002	1.6892	1.6875	1.6842	1.6801	1.6850
$d_{(10\bar{1}4)}$, ± 0.001Å	2.887	2.887	2.885	2.887	2.886
$d_{(0006)}$, ± 0.002Å	2.670	2.671	2.671	2.671	2.668
V_M, ± 0.03 cc.	64.46	64.43	64.26	64.43	64.42
Density, calculated	2.906	2.897	2.874	2.872	2.891
Density, measured	2.82**	2.84**	—	2.86†	2.89†

* All numbers refer to the same samples as in table 1.

** A. H. Chidester, private communication, 1954.

† Average of measurements on a Berman Balance.

The data of table 2 were analyzed by the least square method, which is statistically sound for random errors. Equations of the form

$$f = A + BX + CY \qquad (5)$$

were fitted to the measurements. Here A, B, and C are constants to be determined, and X and Y are independent variables, which are chosen to be the mole fractions of $CaCO_3$ and $MgCO_3$ (to be abbreviated N_{Ca} and N_{Mg} hereafter). The resulting equations are:

$$d_{(10*4)} = 2.886 + 0.06180\Delta N_{Ca} - 0.00836\Delta N_{Mg} \pm 0.0002\text{Å} \quad (6a)$$

$$n(O) = 1.6807 - 0.24916\Delta N_{Ca} - 0.19423\Delta N_{Mg} \pm 0.0007 \quad (6b)$$

$$V_M = 64.344 + 4.153\Delta N_{Ca} - 1.703\Delta N_{Mg} \pm 0.013 \text{ cc.} \quad (6c)$$

where the constant terms correspond to the predicted physical constants for pure, stoichiometric dolomite, $CaMg(CO_3)_2$, and where the $\pm$ values refer to the standard deviations on the five samples, indicating the closeness of fit of the equations to the original data.

Rearrangement of equations (6) gives the final desired results:

$$N_{Ca} = 13.7888d - 0.5935n - 38.2974 \pm 0.0028 \quad (7a)$$

$$N_{Mg} = 58.9233 - 17.6885d - 4.3873n \pm 0.0076 \quad (7b)$$

$$V_M = 87.389d + 5.008n - 196.281 \pm 0.035 \text{ cc.} \quad (7c)$$

Equations (7a) and (7b) are graphically presented in figure 1, in which the five analyzed dolomites are also plotted for comparison.

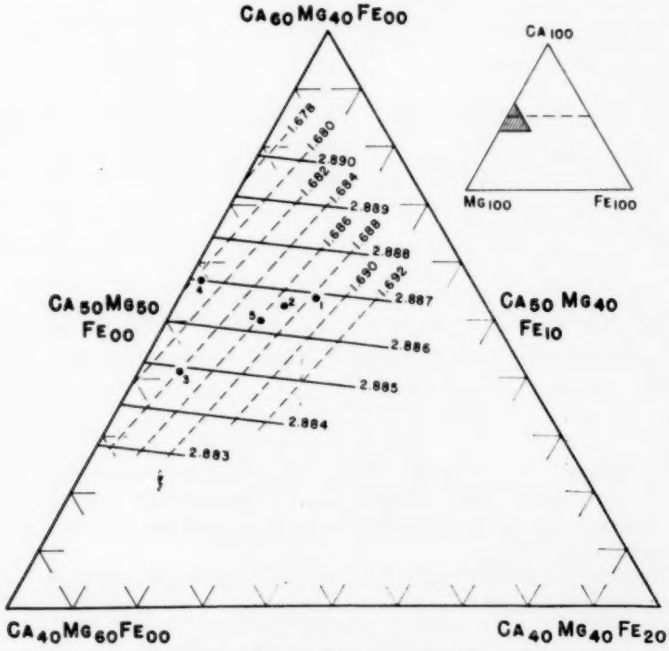

Fig. 1. Relation between ordinary index of refraction (n(O)), (10*4) spacing (Å), and composition of dolomite. Solid lines: *d*-spacing; dashed lines: refractive index.

The results should be checked against other dolomites of known composition for confirmation. Unfortunately, such samples are not available at the present time. We can, however, at least check the internal consistency of the equations, by measuring the volumes of dolomites directly and comparing the results with those derived from equation (7c). This has been done for seven dolomites from calcite-dolomite limestones in low-grade metamorphic terranes. The data are given in table 3. Samples A through E were collected by the writer during a regional geologic survey of the Castleton area, Vermont, and samples F and G, from the Littleton area, New Hampshire, were kindly supplied by Professor M. P. Billings of Harvard University (Billings, 1937, p. 557).

We see from table 3 that the agreement between measured and calculated molar volumes is excellent for all the samples, possibly fortuitously so. The differences shown appear to be random, and are all well within the limits of errors of the equations and measurements. Thus equations (7) may be used with some degree of confidence when the samples are in the neighborhood of pure magnesium dolomite.

TABLE 3

Data on Dolomites from Low-Grade, Two-Carbonate Rocks

Specimen number	Calculated composition	V_M, observed ±0.03 cc.	V_M, calculated ±0.04 cc.	$V_{obs.}$-$V_{cal.}$
A	$Ca_{.54}Mg_{.44}Fe_{.02}$	64.65	64.61	+0.04
B	$Ca_{.50}Mg_{.48}Fe_{.01}$	64.39	64.35	+0.04
C	$Ca_{.55}Mg_{.43}Fe_{.02}$	64.68	64.69	-0.01
D	$Ca_{.50}Mg_{.48}Fe_{.01}$	64.52	64.52	0.00
E	$Ca_{.60}Mg_{.37}Fe_{.03}$	64.96	64.96	0.00
F	$Ca_{.53}Mg_{.43}Fe_{.03}$	64.49	64.53	-0.04
G	$Ca_{.55}Mg_{.42}Fe_{.03}$	64.68	64.70	-0.02

VOLUME RELATIONS IN DOLOMITE

Equation (6c) is useful in yielding additional properties on dolomite, in that from it the partial molar volumes of the components, defined by the relation

$$\overline{V}_i = \left(\frac{\delta V}{\delta n_i}\right)_{n_j} \tag{8}$$

can be obtained. Partial molar volumes are significant quantities, for they tell us how the mean molar volume of the solution changes with composition. Before considering these properties, however, it will be desirable to derive a few general relations.

Consider a system for which an extensive property, Y (Y may be volume, for example), is defined by

$$Y = \sum_{i=1}^{3} n_i \frac{\delta Y}{\delta n_i} = \sum_{i=1}^{3} n_i \overline{Y}_i \tag{9a}$$

and the mean molar value of Y, therefore, by

$$Y_M = \sum_{i=1}^{3} N_i \bar{Y}_i \tag{9b}$$

where n_i is the number of moles of component i in the system, and N_i its mole fraction.

Now at constant T and P, we have the following relation for three components,

$$N_1\left(\frac{\delta \bar{Y}_1}{\delta N_1}\right)_{N_2,T,P} + N_2\left(\frac{\delta \bar{Y}_2}{\delta N_1}\right)_{N_2,T,P} + (1-N_1-N_2)\left(\frac{\delta \bar{Y}_3}{\delta N_1}\right)_{N_2,T,P} = 0 \tag{10a}$$

but from (9b) we have

$$\left(\frac{\delta Y_M}{\delta N_1}\right)_{N_2,T,P} = N_1\left(\frac{\delta \bar{Y}_1}{\delta N_1}\right)_{N_2,T,P} + N_2\left(\frac{\delta \bar{Y}_2}{\delta N_1}\right)_{N_2,T,P} + (1-N_1-N_2)\left(\frac{\delta \bar{Y}_3}{\delta N_1}\right)_{N_2,T,P} + \bar{Y}_1 - \bar{Y}_3 \tag{10b}$$

Hence we obtain

$$\left(\frac{\delta Y_M}{\delta N_1}\right)_{N_2,T,P} = \bar{Y}_1 - \bar{Y}_3 \tag{11a}$$

Similarly, differentiating with respect to N_2,

$$\left(\frac{\delta Y_M}{\delta N_2}\right)_{N_1,T,P} = \bar{Y}_2 - \bar{Y}_3 \tag{11b}$$

Substitution of (11a) and (11b) into (9b) yields the relations:

$$\bar{Y}_1 = Y_M + (1-N_1)\left(\frac{\delta Y_M}{\delta N_1}\right)_{N_2,T,P} - N_2\left(\frac{\delta Y_M}{\delta N_2}\right)_{N_1,T,P} \tag{12a}$$

$$\bar{Y}_2 = Y_M + (1-N_2)\left(\frac{\delta Y_M}{\delta N_2}\right)_{N_1,T,P} - N_1\left(\frac{\delta Y_M}{\delta N_1}\right)_{N_2,T,P} \tag{12b}$$

and

$$\bar{Y}_3 = Y_M - N_1\left(\frac{\delta Y_M}{\delta N_1}\right)_{N_2,T,P} - N_2\left(\frac{\delta Y_M}{\delta N_2}\right)_{N_1,T,P} \tag{12c}$$

Identifying Y with the total volume of the system, we obtain the equations for the partial molar volumes of the three components in dolomite, since we also have from (6c) the relations

$$\left(\frac{\delta V}{\delta N_{Ca}}\right) = 4.153 \text{ cc}$$
$$\left(\frac{\delta V}{\delta N_{Mg}}\right) = -1.703 \text{ cc} \tag{13}$$

Substituting (13) into (12) and using the compositions given in table 1, we obtain, finally,

$$(\bar{V}_{CaCO_3})_{av.} = 33.64 \pm 0.001 \text{ cc} \tag{14a}$$
$$(\bar{V}_{MgCO_3})_{av.} = 30.71 \pm 0.002 \text{ cc} \tag{14b}$$
$$(\bar{V}_{FeCO_3})_{av.} = 31.56 \pm 0.001 \text{ cc} \tag{14c}$$

where the average is over the five sets of dolomite analyses and the standard deviations give a measure of the coherence of data. The values of $\overline{V}_i$ in (14) are half of those given by (12), since (12) corresponds to the "double formulae" for dolomite.

These partial molar volumes, even in infinitely dilute solutions corresponding to use of the approximate equations (4), do not agree with the molar volumes of the same components in calcite, magnesite, and siderite (and rhodochrosite). For these end-members, molar volumes have been calculated, using the data of Andrews (1950, p. 87) for pure calcite, and the data in Palache, Berman, and Frondel (1951, p. 162, 167) for natural magnesite and siderite:

$$V_{CaCO_3} = 36.94 \pm 0.01 \text{ cc.}$$
$$V_{MgCO_3} \sim 28 \pm 0.6 \text{ cc.}$$
$$V_{FeCO_3} \sim 30 \pm 0.5 \text{ cc.}$$

The sum of V_{CaCO_3} and V_{MgCO_3} is 64.9 cc. which is close to the sum of the corresponding partial molar volumes, 64.4 cc. This fact is doubtless responsible for the prevailing notion that the volume effect of the two end-members in the $CaCO_3$–$MgCO_3$ system is additive throughout the composition range, including the intermediate compound dolomite. We now see that this is a coincidence; a conclusion strengthened, moreover, by the fact that the molar volume of pure magnesite is not even known.

PETROLOGIC APPLICATIONS

Limestones and marbles having both calcite and dolomite, but without other minerals having these same components, are interesting for several reasons. Precise information on the compositions of each of the two coexistent carbonates, in a rock of given bulk composition, is of itself of mineralogic interest. In addition, it furnishes empirical data to which any theory of solutions of the carbonates must conform.

Study of coexistent carbonates is of considerable petrologic interest, for this mineral pair is potentially capable of yielding information on the actual physical environment in which the crystallization process took place, provided, of course, that the compositions of the phases are quenchable. We shall now amplify this statement.

Two carbonates in equilibrium are, by definition, mutually saturated with respect to all components. These two phases must, therefore, lie on a solvus. Since increase in solubility of any component in a given phase leads to an increase in entropy, such an increase in solubility generally accompanies rising temperature. Thus the isobaric temperature-composition (T-N) projection of the solvus converges with rising temperature, a fact familiar to most mineralogists.[3]

[3] Readers unfamiliar with thermodynamic concepts may refer to Guggenheim (1950). The following qualitative argument should also help. When temperature and pressure are used as independent variables of state, conditions of thermodynamic equilibrium are specified by minimizing the Gibbs Free Energy function,

$$G = E + PV - TS$$

where E is the internal energy, P the total pressure, V the total volume, T the absolute temperature, and S the entropy; and where it can be shown that

$$\left(\frac{\delta G}{\delta T}\right)_P = -S$$

The shape of the isothermal P-N projection of the solvus, on the other hand, depends on the relative magnitudes of the partial molar volumes of the various components in the two phases, and all that can be said now is that pressure will cause an increase in solubility if and only if such a process decreases the total volume of the system. This fact, however, shows the significance of the partial molar volumes, which are measures of rate of change of the volume of the system upon changes in composition of each of the phases.

If, in addition, the volume change of component i in going from phase α to phase β differs from that of j (for a binary system), i.e.,

$$\Delta\overline{V}_i = |\ \overline{V}_i^{\alpha} - \overline{V}_i^{\beta}\ | \neq |\ \overline{V}_j^{\alpha} - \overline{V}_j^{\beta}\ | = \Delta\overline{V}_j \qquad (15)$$

then the pressure coefficient of solubility differs for the two phases, and successive T-N projections of the solvus will change *shape* as well as relative *location* (fig. 2). For such a system, the determination of the compositions of both coexistent phases would then yield unique information on both the temperature and pressure of recrystallization.[4]

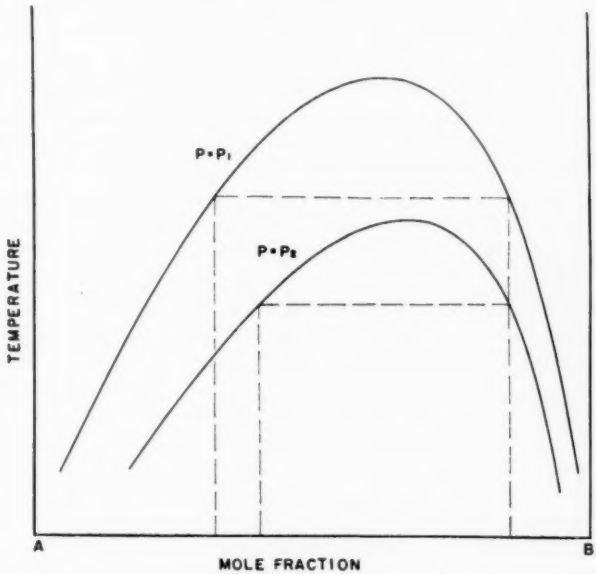

Fig. 2. Diagram showing effect of pressure on solvus sufficient to yield numerical information on the physical variables (see text for explanation).

[4] The above statement is limited by the approximation that Fe and Mn may be treated as one component. The generalization to be made, were this not the case, is obvious.

Since S is intrinsically positive, Gibbs Free Energy decreases with rising temperature (at constant pressure); this decrease will be augmented by an amount corresponding to the entropy of mixing if extra solution takes place.

Our data on the partial molar volumes in dolomite strongly suggest that condition (15) is satisfied. Since these two phases belong to a ternary system, the number of phases, ϕ, is two and the number of components, c, is three, the thermodynamic degree of freedom, f, given by the Gibbs Phase Rule,

$$f = c + 2 - \phi$$

is three; three independent mole fractions must be known in order to fix the state of the system completely. Equations (7a) and (7b) yield two of these; the third mole fraction can be similarly obtained when the calcite system is studied.

Utilization of the above method depends, of course, ultimately on the accumulation of experimental data on the P-T-N relations of the calcite-dolomite system. Experimental work is currently being carried out in several laboratories; these data are awaited with interest.

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DISCUSSION

TABLE MOUNTAINS AND "TUYAS"

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W. H. Mathews (1947) described in this JOURNAL a number of flat-topped, steep-sided volcanoes from northern British Columbia, which he called "tuyas." These "tuyas" bear great resemblance to the "table mountains" of northern Iceland, recently described by the authors (1955).

As Mathews suggests (p. 569-570) that confirmation of his hypothesis on the origin of tuyas might be obtained by a study of the Icelandic "table mountains," the following remarks to this purpose can be offered.

Both tuyas and table mountains, were formed by volcanic eruptions in "intraglacial" lakes, thawed through the ice cover by volcanic heat.

In their lower parts these flat-topped volcanoes consist of granulated material of basaltic composition with a few pillows or basalt globes near the top, whilst they are covered by some flat-lying basalt flows, a few tens to almost 100 feet in thickness.

There is only one apparent difference between tuyas of British Columbia and the table mountains of Iceland. According to Mathews' descriptions, the poorly consolidated fragmental material dips outward from one or more points within the tuya with inclinations of about 30° (Isspah Butte, for instance), whereas the authors found only level strata—or no stratification at all in the palagonitic tuffs and breccias which form the base of the Icelandic table mountains.

However, strong inclinations do also occur in the stratified "pseudo-palagonites" of Iceland, which form a cover of recemented scree material along the sides and slopes of the table mountains. These pseudo-palagonites may completely conceal the underlying palagonite tuffs. They dip outward at about the same angle as the slopes (about 30°), forming a series of stratified layers up to several tens of meters thick. They are of recent formation and rest upon the present-day topography of the mountain's slope, but at a distance the "pseudo-palagonites" may strikingly resemble primary dips of clastic beds of a volcanic cone.

The accompanying photograph, made by the junior author in 1953, shows a cover of such "pseudo-palagonites" on the southern slope of Armannsfell, north of Thingvellir, in the southwestern part of the Central Icelandic graben. They were extensively studied by both authors in 1950, during their Odádahraun expedition, in the northern part of the Central Icelandic graben. As these stratified covers of volcanic tuffs and breccias on secondary sites at first in the field were mistaken by them for volcanic ejectamenta on primary sites, they suppose that the dips observed by Mathews in the slopes of tuyas in northern British Columbia belong also to recemented scree deposits of volcanic tuffs and breccias on secondary sites; the clastic volcanic deposits at primary sites in the core of the tuyas might also be unstratified or of an almost horizontal stratification. If so, the genesis of the tuyas might be completely analogous to that of the Icelandic table mountains, as described by the authors (1955, chap. 7, figs. 41 and 42).

PLATE 1

Cover of "pseudo-palagonites" on the southern slope of Armannsfell, north of Thingvellir, southwestern part of Central Icelandic graben. Photograph, M. G. Rutten.

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COMMENTS

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The following observations from the original field study of tuyas in 1942 are pertinent:

(1) Glacial erosion still proceeding on the north flank of Kawdy Mountain has worked back several hundred feet from the original outer surface of the volcano exposing throughout this distance inclined beds striking at an appreciable angle to the present cirque wall.

(2) No flat-lying beds have been revealed beneath the basalt cap, either at Kawdy Mountain or at any of the other somewhat less dissected tuyas.

(3) Those inclined beds which were regarded as being in situ extend up to a rather well defined line at the base of the basalt cap rather than lapping up to varying elevations over the outcrops of the basalt cap, as they would were they a secondary talus deposit.

These observations suggest that the inclined beds now exposed on the outer slopes of the volcanoes are truly part of the core rather than superficial talus.

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